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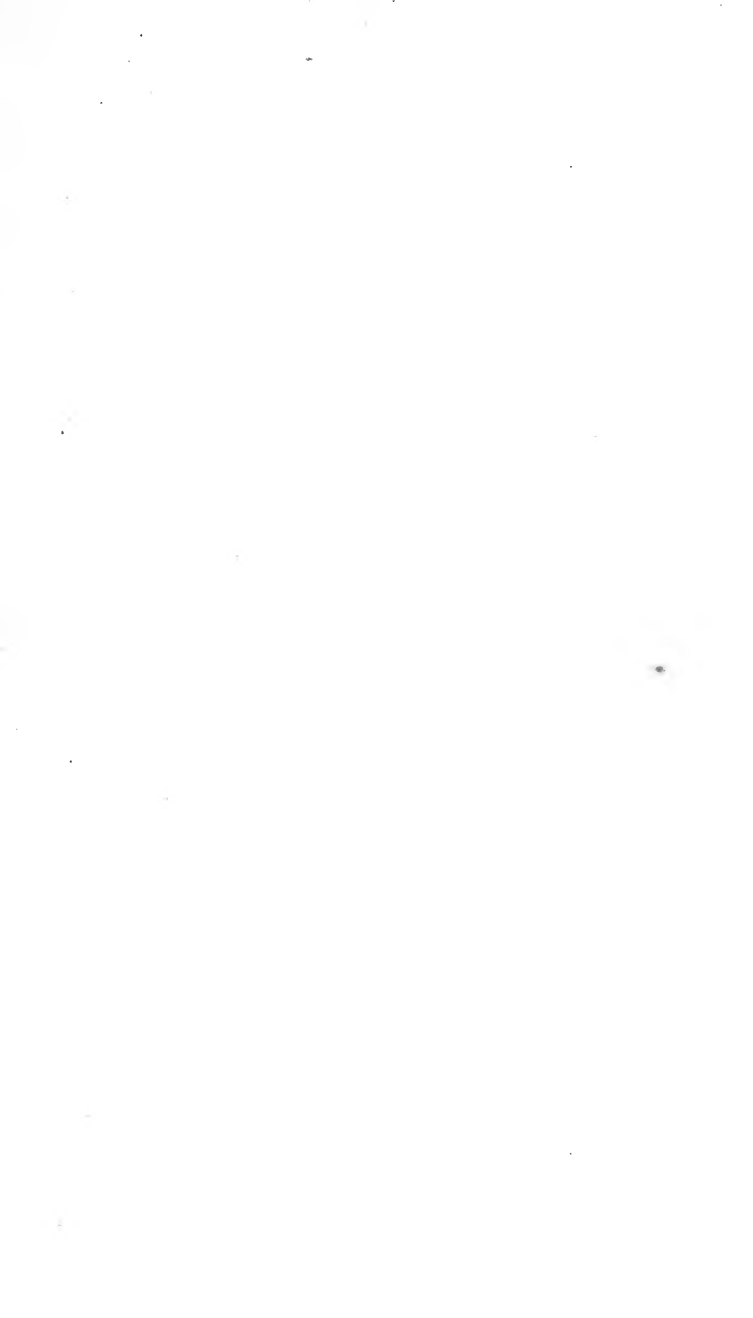
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AMERICAN CHEMICAL JOURNAL

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IRA REMSEN

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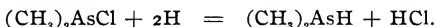
AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the University of Illinois.

SECONDARY ARSINES.

BY WILLIAM M. DEHN AND BURTON B. WILCOX.

The first secondary arsine, dimethylarsine or cacodyl hydride, was prepared by Palmer.¹ He reduced cacodyl chloride by means of platinized zinc and hydrochloric acid, in alcoholic solution, the reaction being :

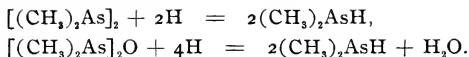


Since the preparation of cacodyl chloride from cacodyl oxide, by treatment with mercuric chloride and hydrochloric acid,² is attended with considerable inconvenience, an easier application of the principle of the general reducibility of alkylated arsenic compounds³ was attempted, *viz.*, the direct reduction of the crude "arsenical liquors of Cadet." It was found that the following reactions took place smoothly and quantitatively, though the yields were, of course, limited by the possibility of condensation of arsine vapors from the excess of hydrogen evolved :

¹ Ber. d. chem. Ges., **27**, 1378.

² Ann. Chem. (Liebig), **107**, 262.

³ THIS JOURNAL, **33**, 105.



Thus a needless operation, that of transforming crude cacodyl into cacodyl chloride, is eliminated, and dimethylarsine can now be prepared with greater ease than any primary or tertiary arsine or any other secondary arsine.

Crude Cacodyl.

This substance, the first known organic compound containing arsenic, was observed by Cadet in 1760, when he distilled a mixture of arsenic trioxide and potassium acetate and obtained a very offensive, heavy, fuming, yellow oil which has since been known as "Cadet's fuming arsenical liquid." In his researches on the cacodyl series, Bunsen¹ found that this substance is a mixture of cacodyl and cacodylic oxide, the latter being present in by far the larger proportion, the former causing the fuming and spontaneous inflammability². No improvement in the yield of this substance has been made since the time of Bunsen, though in 1858 Baeyer³ made experiments with this end in view. By proceeding in the manner described below, we have been able to obtain yields somewhat larger than 30 per cent; these yields, however, include cacodyl, cacodylic oxide and cacodylic acid, all of which are usable for the preparation of dimethylarsine.

An intimate mixture of 250 grams of arsenic trioxide and 250 grams of anhydrous potassium acetate is heated in a short-necked, hard glass flask, of about 500 cc. capacity. The flask is placed in a hemispherical iron cup containing a little sand and is then connected, through a Liebig condenser, with a filter flask used as a receiver. It is advisable to surround the receiver with ice water and to connect its exit-tube with wash bottles containing mercuric oxide, so that all of the crude cacodyl may be condensed or oxidized to cacodylic acid and thus be completely retained. During the course of 8-10 hours, or until the evolution of carbon dioxide ceases and no

¹ Ann. Chem. (Liebig), **37**, 6.

² *Ibid.*, **37**, 6.

³ *Ibid.*, **107**, 261.

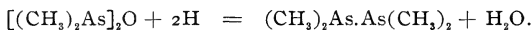
more distillate is collected, the temperature of the flask containing the potassium acetate and arsenic trioxide is gradually raised and continued at a dull red heat. The distillate is found to have collected and separated into 3 distinct layers; the lowest layer, small in quantity, is composed of reduced arsenic or polymerized products (*vide* p. 10); the middle layer, a dark yellow oil, consists of cacodyl and cacodylic oxide; and the upper layer, largest in volume, contains a solution of cacodylic oxide in acetone, acetic acid and water. The second layer is conveniently separated and used directly for the preparation of dimethylarsine; the upper layer is treated with mercuric oxide and, together with the contents of the wash bottles, is filtered and evaporated to a small volume, when it can be reduced to dimethylarsine. By the most careful and intense heating the largest yield of cacodylic oxide was 25 per cent.; the amount of cacodylic acid obtained increased the yield so that it exceeded 30 per cent.

Reduction of Cacodylic Oxide to Dimethylarsine.

The reduction of cacodylic oxide to dimethylarsine is conducted in a manner similar to that employed in the preparation of methylarsine. Amalgamated zinc dust (250 grams), cacodylic oxide (50 grams) and alcohol (200 cc.) were placed in a 1-liter, round-bottomed flask, to which were connected in order, a water wash bottle, a U-tube filled with soda-lime, the condenser used for methylarsine,¹ a sulphuric acid wash bottle and a nitric acid wash bottle. The connections were made of glass and cork throughout, because the arsines attack rubber with great avidity. After surrounding the condensing bulbs with a freezing mixture of salt and ice, concentrated hydrochloric acid is slowly admitted to the reduction flask, through a dropping funnel. After a few minutes a bright yellow substance forms and indicates a partial reduction; this color disappears as the reduction proceeds. Some little time intervenes between the beginning of the evolution of the hydrogen and the passage of the dimethylarsine. The beginning of the evolution of the arsine is detected when the passage of the evolved

¹ Ber. d. chem. Ges., 34, 3594.

gases is faster through the wash bottle next to the reduction flask than it is through the sulphuric acid bottle beyond the condensing apparatus. This period of time intervening between the beginning of the reduction and the evolution of the arsine is undoubtedly consumed in the reduction of the cacodylic oxide to cacodyl—the intermediate product of the reduction :



This period of time is longer when cacodylic acid is used instead of crude cacodyl; the former requires 6 atoms of hydrogen, the latter requires 2-4 atoms of hydrogen, depending upon the relative proportions of the cacodyl and cacodylic oxide present.

When the apparatus contains air a red body is always formed on the inner surfaces of the apparatus. This substance is similar in composition to the red compounds formed in the Wurtz condensations to be mentioned further on and discussed under oxidations (*vide* p. 10).

As the reduction proceeds liquid arsine may be drawn off from the condenser bulbs and sealed in bulbs or constricted test tubes. In this manner 50 grams of cacodyl may be reduced in the course of 2 hours. Occasional shaking of the reduction flask is necessary because the cacodyl coats the zinc and prevents the action of the hydrochloric acid.

Dimethylarsine is a colorless, mobile liquid having the characteristic odor of cacodyl. It is very volatile and inflames in air at a temperature above 10° but not below 0°, burning with a blue-white arsenical flame and giving rise to white fumes and a black, solid deposit. It boils at 35°.6 (747 mm.) and at 55° under 1.74 atmospheres pressure.¹ Its sp. gr. is 1.213 at 29°.

The purity of the arsine used in the following studies is shown by the result of a molecular weight determination by Hofmann's method :

0.5794 gram $(\text{CH}_3)_2\text{AsH}$ gave 169 cc. vapor at 99°.3 and 750 mm.

¹ THIS JOURNAL, 33, 123.

Mol. wt.	Calculated for (CH ₃) ₂ AsH. 106.0	Found. 105.7
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Like methylarsine,¹ dimethylarsine is soluble in alcohol, ether, chloroform, carbon bisulphide, benzene, etc., in all proportions. In fact, it resembles very closely the lower fatty primary arsines in their physical properties and most of their chemical reactions. In one particular it differs remarkably from the fatty primary arsines; whereas, the latter fume and inflame only on warming, dimethylarsine inflames spontaneously in the air, at a temperature almost as low as 0°. This same difference of ease of oxidation is seen also in the case of phenyl and diphenylarsines; the latter can be isolated only with the greatest difficulty by the method employed for the preparation of phenylarsine, on account of this great affinity for oxygen.

General Reactions of Dimethylarsine.

Dimethylarsine reacts with the greatest of ease with inorganic substances, such as the halogens, the halogen acids and their heavy metal salts, with oxygen and sulphur, with oxides and sulphides and with oxygenated acids and salts. Of the organic compounds affected by dimethylarsine, reactions with alkyl halides and reactions in which the arsines can exert a reducing effect have been studied the most. It may be said, in general, that only a few of the many reactions proposed and studied have failed to give definite transformations.

The reactions of the arsines may be divided into two general classes, *viz.*, those that involve

1. Addition,
2. Addition and subsequent dissociation,

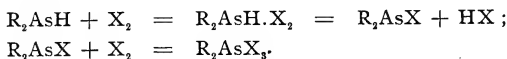
or, in other words, reactions which involve a change from

1. Trivalent arsenic to pentavalent arsenic,
2. Pentavalent arsenic to trivalent arsenic.

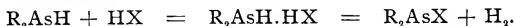
Theoretically, all the reactions of the arsenic compounds may be explained on one or the other of these hypotheses.

¹ THIS JOURNAL, 33, 172.

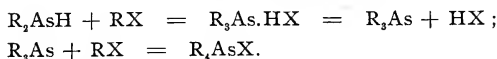
With halogens, secondary arsines successively form compounds of the types $R_2AsH.X_2$, R_2AsX and R_2AsX_3 , according to the equations :



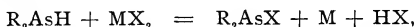
With halogen acids, either $R_2AsH.HX$ or R_2AsX , according to the equation :



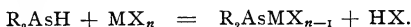
With alkyl iodides, compounds of the types $R_2AsH.RX$, R_3As and R_4AsX , according to the equations :



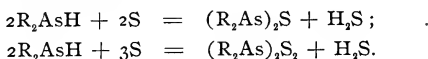
With halogen salts of the heavy metals, compounds of the type R_2AsX :



or, with the elimination of the halogen acid, compounds of the type R_2AsMX_n :



With the metalloids, such as sulphur, compounds of the types $(R_2As)_2S$ and $(R_2As)_2S_2$:



With oxygen, compounds of the types $R_2As.AsR_2$, R_2AsO , AsR_2 and R_2AsOOH (*vide* oxidation of dimethylarsine, p. 9) and with oxygenated acids and salts, the oxidation products of arsine mentioned above, and the various reduction products of the acids and salts.

Method of Controlling Reactions.

On account of the spontaneous inflammability of dimethylarsine it was necessary to employ special methods for conducting and studying the reactions. The arsine, when prepared, was sealed in small bulbs or constricted test tubes. These

tubes were placed in ordinary bomb tubes, together with a heavy glass rod and the reagent, which was usually sealed in separate bulbs.

The bomb tubes were then constricted at the open end, cooled and filled with carbon dioxide passed in through capillary tubes, or, when ether was used as a medium for the reactions, the air contained in the bomb tubes was easily displaced by distilling out a portion of the ether. When filled with carbon dioxide or with ether vapor the tubes were sealed.

When slow regulated reactions were desired, or when danger of explosion was to be avoided, by careful agitation of the glass rod only the capillary tubes of the bulbs containing the arsine were broken.

Methods of Analysis.

In addition to the usual methods of analysis the following were employed :

Method (a). Analysis of many of the compounds containing halogen was greatly facilitated by the application of Volhard's method of titration. It was found that the halogen atoms linked directly to arsenic were easily removed by boiling with silver nitrate and nitric acid. The excess of silver nitrate used was titrated by means of thiocyanate, with ferric nitrate as an indicator. Preliminary analyses of arsenic trichloride, phenylarsine chloride and tetraethylarsonium iodide, by this method, gave quantitative results.

Method (b). Treatment of the substance with an excess of sodium peroxide¹ separated the arsenic from its organic groups and the former could be determined quantitatively by the usual methods.

Method (c). To determine the presence of inorganic arsenic, or the $\text{RAs}\equiv$ and $\text{R}_2\text{As}\equiv$ groups, the substance was first oxidized by chlorine or bromine water, then treated with magnesia mixture—a precipitate in the cold indicates inorganic arsenic (though possibly derived from RAs), a precipitate on boiling, the $\text{RAs}\equiv$ group; and a solution, which with zinc and hydrochloric acid evolves vapors having the fuming and

¹ THIS JOURNAL, 31, 386.

odor of the arsines, indicates the presence of $R : As \equiv$ group. In the presence of nitrates, chlorates, etc., the evolution of the arsines will often be retarded or suppressed.

Method (d). Another method for the detection of these constituents makes use of hydrogen sulphide, in hydrochloric acid solution; a yellow, solid precipitate indicates inorganic arsenic; a slowly forming, light yellow, gummy oil¹ indicates RAs , and the immediate formation of a white emulsion or a colorless oil, $(R_2As)_2S$, indicates the presence of the $R_2 : As \equiv$ group.

Method (e). The presence of arsenic, either organic or inorganic, can be detected by treating with zinc and hydrochloric acid; the vapors evolved can usually be differentiated by the sense of smell.

Method (f). In gaseous mixtures the volume of arsenic present was determined by treatment with silver nitrate solution² (*vide* p. 34).

Decomposition of Dimethylarsine by Heat.

A bulb of 1.07 grams of dimethylarsine was sealed in a bomb tube (52 cc. capacity) from which the air was exhausted to 25 mm. pressure, and was then broken by the glass rod. A slight fuming indicated the presence of only a trace of air. The bomb tube was exposed to direct sunlight during 2 weeks³ and was then heated for an hour at 192° , and for 2 hours at 242° , but no evident change took place. After the tube had been heated for an hour at 335° , it was found that the entire inner surfaces of the tube were covered by a beautiful, shining, black, metallic mirror. Upon opening the tube 46.6 cc. of gas were collected and treated with silver nitrate; a decrease in volume of 10.1 cc. resulted, therefore 21.6 cc. of the gaseous products were unchanged arsine. The gas remaining after treatment with silver nitrate (36.5 cc.) burned with a blue flame and gave no easily explosive mixture with air—it was evidently methane or a mixture of ethane and hydrogen. The metallic deposit was washed with potassium hydroxide solution, then with water and dried at 122° .

¹ THIS JOURNAL, 33, 133.

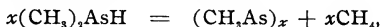
² *Ibid.*, 33, 144.

³ Cf. Arsine itself. J. prakt. Chem., 6, 346. Compt. rend., 93, 615. Ann. Chim. Phys., [5], 20, 20.

0.0430 gram was dissolved in bromine water and treated with magnesia mixture : 0.0829 gram $\text{Mg}_2\text{As}_2\text{O}_7$ resulted :

	Calculated for $(\text{CH}_3\text{As})_x$.	Found.
As	82.63	83.33

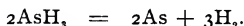
This black, metallic, arsenic-like substance gave good tests for carbon, therefore it is evidently the black polymer mentioned by Auger,¹ and the reaction indicating the decomposition of dimethylarsine by heat is :



or



When arsine is heated to 230° it begins to decompose² and, at a red heat, is completely resolved according to the equation :³



A more complete study of the decomposition of the arsines will be made during the year.

Oxygen and Dimethylarsine.

When dimethylarsine is treated with pure or atmospheric oxygen, any or all of the following reactions may take place :

1. $6(\text{CH}_3)_2\text{AsH} + 3\text{O}_2 = (\text{CH}_3\text{As})_4\text{As}_2\text{O}_3 + 4\text{C}_2\text{H}_6 + 3\text{H}_2\text{O}.$
2. $4(\text{CH}_3)_2\text{AsH} + \text{O}_2 = 4(\text{CH}_3\text{As})_x + 2\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}.$
3. $4(\text{CH}_3)_2\text{AsH} + \text{O}_2 = \text{As}_4 + 4\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}.$
4. $2(\text{CH}_3)_2\text{AsH} + 9\text{O}_2 = \text{As}_2\text{O}_3 + 4\text{CO}_2 + 7\text{H}_2\text{O}.$
5. $4(\text{CH}_3)_2\text{AsH} + \text{O}_2 = [(\text{CH}_3)_2\text{As}]_2 + 2\text{H}_2\text{O}.$
6. $2(\text{CH}_3)_2\text{AsH} + \text{O}_2 = [\text{CH}_3)_2\text{As}]_2\text{O} + \text{H}_2\text{O}.$
7. $(\text{CH}_3)_2\text{AsH} + \text{O}_2 = (\text{CH}_3)_2\text{AsOOH}.$

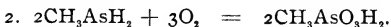
When methylarsine⁴ was treated with oxygen the following reactions occurred :

¹ Compt. rend., 138, 1707.

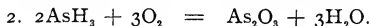
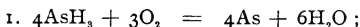
² Ber. d. chem. Ges., 22, 3202.

³ Compt. rend., 93, 617. J. prakt. Chem., 6, 347. Ann. Chim. Phys., 43, 407.

⁴ THIS JOURNAL, 33, 124.



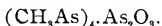
The following reactions of arsine¹ with oxygen have been reported :



Evidently the affinity of the arsines for oxygen increases with the number of alkyl groups introduced; for arsine itself does not unite, at ordinary temperatures, with oxygen, primary arsines do, but not with the spontaneous inflammability which characterize the secondary and tertiary arsines.

All of the above oxidation products of dimethylarsine, except cacodyl, have been identified. On account of its spontaneous inflammability, it has been found impossible to isolate it from the oxidation product, however, since it is often found as a product of oxidation when liquid oxidizing agents are employed, it is easy to see that it is probably formed when gaseous arsine is treated with diluted oxygen or mild oxidizers.

When dimethylarsine is permitted to oxidize slowly in the air, there is always formed a bright red solid, which is probably identical in composition with "erytrarsine" described by Bunsen,² whose data indicate a compound of the formula



Evidence for the presence of the loosely bound inorganic arsenious oxide and of the CH_3As group is seen in the following. The substance was washed repeatedly with water and then with alcohol, to remove any adhering cacodylic acid or cacodylic oxide and was then dissolved in bromine water; upon making ammoniacal and adding magnesia mixture a copious precipitate of $\text{NH}_4\text{MgAsO}_4$ was obtained.

After filtering, acidifying with hydrochloric acid and treating with hydrogen sulphide there was formed a precipitate of

¹ Ann. Chim. Phys., **33**, 355; **43**, 407. J. prakt. Chem., **6**, 347. Comment. Soc. Gött., **16**, 141. Ber. d. chem. Ges., **22**, 3203.

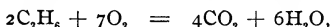
² Ann. Chem. (Liebig), **42**, 41.

CH_3AsS_2 , recognized by its oily consistency and its characteristic odor.¹

When dimethylarsine is treated with pure oxygen, or when warmed and treated with concentrated oxygen, the reaction gives rise to a flame and the immediate formation of a black solid, which has been proved to be a mixture of $(\text{CH}_3\text{As})_x$ ² and metallic arsenic. Evidence for the presence of the CH_3As grouping was derived in the manner described above for the red polymer. In fact this black polymer can be obtained from the red polymer by heating.³ The red and black polymers are insoluble in dilute alkalies; the solid resulting from the flame reaction can be proved to contain arsenious acid, by dissolving in dilute alkalies and testing in the usual manner.

Proof of the formation of metallic arsenic⁴ was obtained as follows: When liquid arsine was dropped into pure oxygen a closely compacted, metallic mirror was formed. On removing and washing it free from cacodylic acid it was found to give no test for carbon, but gave all of the usual tests for metallic arsenic.

The formation of ethane was proved thus: The gas resulting from a flame reaction was obtained in a eudiometer over mercury and treated, successively, with alkaline pyrogallol to remove oxygen, with silver nitrate to remove unchanged arsine, and with bromine water to remove unsaturated hydrocarbons (such have not been found). The residual gas was found to burn with quite a luminous flame and to give no deposit of metallic arsenic on cold porcelain. When 11.8 cc. of the residual gas, known to contain nitrogen, were treated with 4.98 cc. of oxygen and exploded in a mercury pipette, a contraction of 2.92 cc. resulted, owing to the formation of water. After treating with potash a further contraction of 2.28 cc. was incurred. According to the equation



¹ Ber. d. chem. Ges., 16, 1441. THIS JOURNAL, 33, 134. Ann. Chem. (Liebig), 249, 134.

² Compt. rend., 138, 1707.

³ Cf. Ann. Chem. (Liebig), 42, 42. Compt. rend., 138, 1707.

⁴ Cf. Primary Arsines. THIS JOURNAL, 33, 124.

the contraction owing to the formation of water is to the contraction owing to the formation of carbon dioxide, as 5 : 4. The ratio found was 2.92 : 2.28, that is, an error of 2 per cent.

The gas resulting from the flame reaction can easily be proved to contain carbon dioxide by passing it through lime water.

In the flame reaction and in all other oxidations of dimethylarsine, cacodylic acid and usually cacodylic oxide can easily be proved to be present in the products. The former was separated by dissolving in water or alcohol and was identified by its crystalline form and melting-point; the latter was detected by its solubility in water and its characteristic, penetrating odor—all of the other substances mentioned above are practically odorless.

It may be said, in general, that cacodylic acid and cacodylic oxide are products of slow oxidation. The former is almost the total product when an ether solution is exposed, through a small orifice, to the action of the air; the latter is abundant when air and arsine are brought together in the presence of water. In either case some of the red polymer mentioned previously may be formed.

Further evidence in proof of the above 7 oxidation reactions is derived from gasometric studies. The following tables give the volumes of arsine and oxygen required by these 7 equations, the resulting volumes and contractions are given in per cents of the arsine and oxygen used.

Equation.	Arsine.	Oxygen.	Resulting.	Per cent of contraction of the	
				Arsine.	Oxygen.
1	6	3	4	83	166
2	4	1	1	100	400
3	4	1	4	25	100
4	2	9	4	350	77
5	4	1	0	125	500
6	2	1	0	150	300
7	1	1	0	200	200

The following reactions were conducted in a nitrometer containing mercury and surrounded by a jacket, through which were passed the vapors of chloroform. All data given below

have been calculated to standard conditions of temperature and pressure :

Experiment.	Arsine.	Oxygen.	Resulting.	Contractions.	Per cent of contraction to arsine.
(a)	17.36	43.51	44.90	15.97	0.92
(b)	22.77	32.71	27.77	27.71	1.22
(c)	20.29	34.37	44.43	30.23	1.49

In experiment (a) a strong flame-reaction resulted, while in (b) less, and in (c) little flame-reaction was observed. Evidently a combination of reactions (2), (3), (6) and (7) with none of (2) and (3) in experiments (a) and (b), and none of (6) and (7) in (c). Further evidence for these conclusions was derived from a study of the oxidation products; no red polymer, carbon dioxide, or cacodyl was found in experiments (a), (b) or (c), therefore reactions (1), (4) and (5) are eliminated; the black polymer, cacodylic oxide and cacodylic acid were found, therefore, necessarily, combinations of (2), (3), (6) and (7) were involved.

When reactions with oxygen, without the flame-reaction, take place, invariably contractions equal in volume to 150-200 per cent of the arsine result; evidently only reactions (6) and (7) are involved under these conditions.

In the following experiments a mixture of hydrogen and arsine was prepared, kept in a suitable gas reservoir, and its per cent of arsine determined by treatment with a solution of silver nitrate.

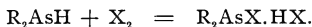
Quantities of the mixture were drawn off into Hempel burettes, measured and treated, either rapidly or slowly, with measured quantities of air; fuming but no flame-reaction resulted; slightly greater contractions were observed upon rapid treatment.

No. of experiment.	Mixture.	Air.	Sum.	Result.	Contraction.	Corrected volume of arsine.	Per cent of contraction of arsine.
1	21.2	69.2	90.4	72.6	17.8	10.6	168
2	26.6	79.8	106.4	84.6	21.8	13.3	164
3	18.6	78.6	97.2	82.1	15.1	9.3	162
4	29.2	75.0	104.2	79.0	25.2	14.6	172
5	16.7	75.0	91.7	77.2	14.5	8.3	174
6	16.0	80.1	96.1	82.2	13.9	8.0	174

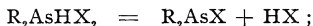
Evidently treatment with atmospheric oxygen gives, as products, approximately equal quantities of cacodylic oxide and cacodylic acid.

Halogens and Dimethylarsine.

When halogens are brought into contact with gaseous or liquid dimethylarsine, there result immediate energetic reactions attended by light, if no diluent is employed; when organic diluents are used, precipitates of the pentavalent addition products are formed, according to the equation:



However, when water is present or the temperatures are too high, the addition products dissociate into trivalent arsenic halides:



thus the products of the action of halogens on dimethylarsine are cacodyl halides or their hydrhalogen salts, except when the halogen is permitted to react at very high temperatures, then flame-reactions take place and there result polymerized or decomposed products similar to those formed by reactions 2, 3 and 4 of oxidation.

Bromine and Dimethylarsine.

When 5.5 grams of dimethylarsine (1 mol.) and 9 grams of bromine (excess of 1 mol.) were brought together in a sealed tube, so that an energetic reaction took place, there resulted a solid mass of dark brown color and a little colorless oil. On standing for some time the solid changed to large, white, tabular crystals and a little dark brown, amorphous solid. On opening the tube considerable pressure was noticed, the gaseous products were collected and were proved to contain hydrobromic acid and hydrogen. The former was identified by absorption in potassium hydroxide solution and treatment with silver nitrate, the latter by its combustibility. To prove the presence of hydrogen, 2.3 cc. of the gas, freed from hydrobromic acid, was exploded with oxygen; a contraction of

3.6 cc. resulted, an error of 3 per cent. The colorless oil was drained from the crystals, filtered and analyzed for halogen :

0.3393 gram substance required 0.4006 gram silver nitrate.

	Calculated for (CH ₃) ₂ AsHBr ₂ .	Calculated for (CH ₃) ₂ AsBr.	Found.
Br	60.20	43.24	55.57

Evidently the oil was a mixture of cacodyl bromide and *bromcacodyl hydrobromide* ; upon standing, crystals of the latter were deposited.

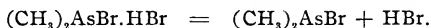
The white crystals, the main product of the action of bromine upon dimethylarsine, were washed with chloroform, separated mechanically from the broken glass and the brown, amorphous solid, dried in a desiccator and analyzed by Volhard's titration method.

I. 0.1508 gram substance required 0.2599 gram AgNO₃.

II. 0.0618 gram substance required 0.0791 gram AgNO₃.

	Calculated for (CH ₃) ₂ AsBr.HBr.	I.	Found.	II.
Br	60.20	60.52		60.26

Bromcacodyl hydrobromide, a white, tabular, crystalline solid, is quite stable in air. It is somewhat soluble in hot chloroform, less so in carbon bisulphide, and is insoluble in ether. It decomposes slowly in cold water and rapidly in hot water and ammonium hydroxide, according to the equation :



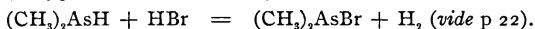
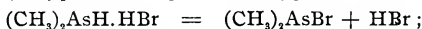
When 6.2 grams of dimethylarsine (1 mol.) and 10 grams of bromine (1 mol.) were brought into contact and their reaction products were immediately decomposed by means of water and then subjected to steam distillation, 2.5 grams of cacodyl bromide were separated.

After removing the cacodyl bromide there was left a dark brown, amorphous solid, which was probably identical with Bunsen's "erytrsine" mentioned above. After boiling repeatedly with water, and drying at 120°, it was analyzed for arsenic.

0.2138 gram substance gave 0.2358 gram Mg₂P₂O₇.

	Calculated for (CH ₃ As) ₄ .As ₂ O ₃ .	Calculated for (CH ₃ As) _x .	Found.
As	80.64	83.33	82.10

The above data justify the following equations to represent the reaction when dimethylarsine is brought into contact with bromine :



The formation of the polymer is cleared up by a study of the action of arsenic trichloride upon dimethylarsine (*vide* p. 40).

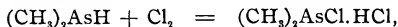
Chlorine and Dimethylarsine.

A quantity of dimethylarsine was placed in a gas wash bottle and treated with a slow stream of dry chlorine ; an immediate flame-reaction took place, attended by a deposition of arsenic and of a black solid polymer. When an excess of chlorine was added, the reaction product became chiefly liquid. The contents of the wash bottle were extracted with chloroform and its solution was dried and distilled. Methylarsine dichloride, CH₃AsCl₂, was found to be the chief constituent of the liquid which boiled at 100°-150° (CH₃AsCl₂ boils at 123° ; (CH₃)₂AsCl boils at 100°). The fraction boiling at 140°-145° was analyzed for chlorine :

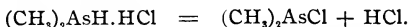
0.1948 gram substance required 0.4208 gram AgNO₃.

	Calculated for (CH ₃) ₂ AsCl.	Calculated for CH ₃ AsCl ₂ .	Found.
Cl	24.93	44.10	44.98

It is probable that chlorine reacted with dimethylarsine, as did bromine, with the formation of *chlorocacodyl hydrochloride*,

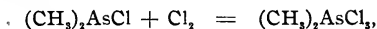


which decomposed at the temperature of the reaction and formed cacodyl chloride,

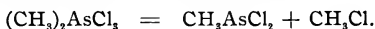


Cacodyl chloride could then react with chlorine according to

the known reaction and form the pentavalent body, dimethylarsine trichloride,



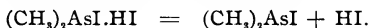
which decomposes at a temperature above 40° – 50° , and forms methylarsine dichloride and methyl chloride,¹



The phenomenon attending the reaction of the chlorine with arsine is very similar to that with dimethylarsine.²

Iodine and Dimethylarsine.

When 2.6 grams of dimethylarsine (1 mol.) were treated in a sealed tube with 6.2 grams of iodine (1 mol.), an immediate reaction took place, with the liberation of much heat and the formation of a yellow solid, which crystallized on standing. Little or no pressure was observed on opening the tube. By washing with chloroform the crystalline substance, *iodocacodyl hydriodide*, $(\text{CH}_3)_2\text{AsI.HI}$, was obtained pure. It crystallizes in large, well-formed, light yellow needles which, when heated rapidly, soften and darken at 160° , and melt at 175° ; by continued heating at 60° the crystals darken and liberate iodine. Iodocacodyl iodide is insoluble in ether and chloroform and soluble in alcohol, with evident decomposition. Water decomposes it easily, according to the equation:



0.1244 gram substance required 0.1299 gram AgNO_3 .

	Calculated for $(\text{CH}_3)_2\text{AsI.HI}$.	Found.
I	70.55	69.90

Iodine decomposes arsine slowly in the cold, rapidly on heating, into hydriodic acid and arsenic trioxide.³

Aqueous Iodine and Dimethylarsine.

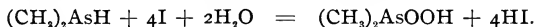
When 0.1848 gram of dimethylarsine was brought into contact with an excess of standard iodine solution and the un-

¹ Ann. Chem. (Liebig), 107, 269.

² Ann. Chim. Phys. [2], 43, 407. Gmelin-Kraut Handbuch der Chemie.

³ Ann. Chim. Phys., [2], 43, 407. Compt. rend., 67, 56. Anal. Zeitschr., 7, 476. Ber. d. chem. Ges., 20, 1099; 21, 2546.

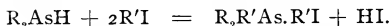
changed iodine titrated with standard thiosulphate solution, the following reaction was found to have taken place :



0.8716 gram of arsine was used, whereas the theory required 0.8916 gram—the error of 2 per cent being accounted for by the difficulty of avoiding oxidation.¹

Alkyl Halides and Dimethylarsine.

In 1854 Landolt² found that triethylarsine reacted with ethyl iodide, slowly in the cold, more rapidly when heated, and formed a crystalline product, tetraethylarsonium iodide, $(\text{C}_2\text{H}_5)_4\text{AsI}$. This reaction was found to be analogous to the formation of tetramethylstibonium iodide, $(\text{CH}_3)_4\text{SbI}$, from trimethylstibine and methyl iodide.³ It was observed by one of us⁴ that when primary arsines were heated with 3 molecules of alkyl iodides, there resulted arsonium iodides of the types $\text{RR}'_3\text{AsI}$ and R_4AsI .⁵ It was stated that the intermediate products $\text{RR}'\text{AsH} \cdot \text{HI}$ and $\text{RR}'_2\text{As} \cdot \text{HI}$ were probably formed, but, being unstable, split off hydriodic acid and added more alkyl iodide, until the arsonium body was produced. We have found that the secondary arsines react with equal ease with the alkyl iodides, forming both the intermediate product $\text{R}_2\text{R}'\text{As} \cdot \text{HI}$ and the end product, the arsonium iodide, according to whether the arsine is allowed to react with 1 molecule of the alkyl iodide in the cold or is heated with 2 molecules :



Dimethyldiisobutylarsonium Iodide.

When 5 grams of dimethylarsine were sealed with 21.7 grams of isobutyl iodide (2.5 mols.) and heated 5 hours, at 110° , there resulted a crystalline mass, colored red by a small amount of arsonium periodides. The solid was extracted from the reaction tube by means of water and heated in a beaker,

¹ Cf. Primary Arsine. *THIS JOURNAL*, **33**, 126.

² *Ann. Chem. (Liebig)*, **89**, 331.

³ *Ibid.*, **84**, 44.

⁴ *THIS JOURNAL*, **33**, 128.

⁵ *Ibid.*, **33**, 115.

on the water-bath, with potassium hydroxide solution, to destroy the periodides and to evaporate the excess of alkyl iodides used. The arsonium iodide separated from the alkali solution as a solid and was removed by filtering on glass wool. It was extracted from the glass wool by means of chloroform and, after drying with calcium chloride, was precipitated by ether as a white, crystalline solid. It is soluble in alcohol and chloroform, but insoluble in ether and melts at 155° .

0.2470 gram substance required 0.1213 gram AgNO_3 .

I	Calculated for	Found.
	$(\text{CH}_3)_2(\text{C}_4\text{H}_9)_2\text{AsI.}$	
	36.70	36.67

Dimethyldicetylarsonium Iodide.

Dimethylarsine (5.94 grams) did not react with 49.3 grams of cetyl iodide (2 mols.) on standing at room temperature. After heating 5 hours, at 100° , the entire mass was changed to a crystalline solid.

The solid was decolorized by boiling with potassium hydroxide, which precipitated it as an oil. It was separated from the alkali solution and dissolved in chloroform. The dry chloroform solution was diluted with much ether and cooled, when the dimethyldicetylarsonium iodide separated as a slightly yellow, crystalline solid. It was obtained perfectly white on recrystallizing. It melts at 53° – 54° .

0.1872 gram substance required 0.0465 gram AgNO_3 .

I	Calculated for	Found.
	$(\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})_2\text{AsI.}$	
	18.62	18.57

Dimethyldiisopropylarsonium Iodide.

Dimethylarsine (4.6 grams) and isopropyl iodide (18 grams, 2.5 mols.), after standing in contact 18 hours, deposited some crystals; after heating for 3 hours, at 100° , the entire mass became solid. The arsonium iodide, freed from arsonium periodides by boiling with potassium hydroxide, was precipitated from the chloroform solution by ether, in the usual manner.

Dimethyldiisopropylarsonium iodide is a pure white, crystalline solid easily soluble in chloroform and very insoluble in ether. It does not melt at 230° .

0.1136 gram substance required 0.0604 gram AgNO_3 .

	Calculated for $(\text{CH}_3)_2(\text{C}_3\text{H}_7)_2\text{AsI}$.	Found.
I	39.93	39.68

Dimethyldiallylarsonium Iodide.

A large excess of allyl iodide (3-4 mols.) reacted very violently with dimethylarsine, liberating sufficient heat to boil the mixture. A precipitate began to form and in less than 30 minutes the entire mass had become solid. On opening the tube in which the reactions had taken place much pressure was observed; vapors of iodine, hydriodic acid, and a gas that burned with a sooty flame were given off. On account of the large excess of allyl iodide it was impossible to separate the arsonium iodide in the usual manner, but crystals dried on clay plates were found to be light yellow in color, soluble in alcohol and insoluble in ether. Analysis:

0.1330 gram substance required 0.0709 gram AgNO_3 .

	Calculated for $(\text{CH}_3)_2(\text{C}_3\text{H}_5)_2\text{AsI}$.	Found.
I	40.44	39.81

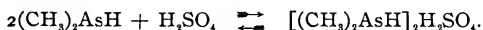
Dimethylallylarsine.

When dimethylarsine (3 grams) was treated with 1 molecule of allyl iodide (4.8 grams) the reaction was not so violent as when 3 to 4 molecules of the allyl iodide were used in the preparation of dimethyldiallylarsonium iodide. As the arsine was slowly added a yellow precipitate was first formed, but it disappeared when all of the arsine came into contact with the reaction mixture. Only a little heat was evolved. On opening the tube a pressure due to hydriodic acid was observed; arsine was absent. The liquid contents were removed and distilled. *Dimethylallylarsine* distilled at about 160° and yielded a clear, light yellow, non-fuming liquid of a strong, disagreeable odor, irritating to the eyes and skin. It was proved to be a tertiary arsine by treatment with 1 molecule of methyl iodide. Crystals

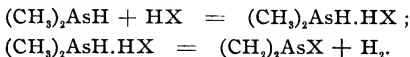
formed at ordinary temperatures ; when heated 1 hour at 75°–80° the entire mass became solid, owing to the production of the trimethylallylarsonium iodide, $(\text{CH}_3)_3(\text{C}_3\text{H}_5)\text{AsI}$. Dimethylallylarsine reacted violently with bromine, in ether solution, and formed a yellow, flocculent precipitate, *dimethylallylarsine dibromide*, $(\text{CH}_3)_2(\text{C}_3\text{H}_5)\text{AsBr}_2$.

Alkalinity of the Arsines.

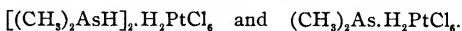
It was stated by one of us¹ that the primary arsines possess weakly basic properties. We have found that the secondary arsines also possess basic properties ; they form, with sulphuric acid, well-defined, crystalline salts which are unstable in moist air ; with halogen acids, salts which are decomposed at ordinary temperatures ; and with platinic chloride, double salts which are analogous in composition to the corresponding amines. The equation for the formation and decomposition of the sulphuric acid salt is as follows :



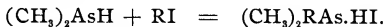
The formation and decomposition of the halogen acid compounds are represented thus :



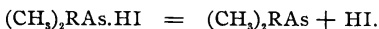
The compounds produced with platinic chloride are



We have found that the tertiary arsines also possess basic properties. This is best seen in the action of alkyl halides upon dimethylarsine,



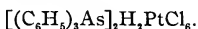
This hydriodic acid salt of the tertiary arsine is quite stable in dry air, but is decomposed by water according to the equation :



In the aromatic series tertiary arsines have been found to

¹ THIS JOURNAL, 33, III.

have some basic properties; Michaelis prepared triphenylarsine hydroplatinic chloride,¹



Dry Hydrobromic Acid and Dimethylarsine.

A bulb of dimethylarsine was placed in a small bottle and the whole was weighed. It was then connected on both sides with U-tubes containing phosphorus pentoxide; to one drying tube was attached an apparatus for the generation of gaseous hydrobromic acid; to the other U-tube, small wash bottles containing solutions of potassium hydroxide and silver nitrate, respectively. The silver nitrate wash bottle was connected to a Hempel burette for the collection of gas.

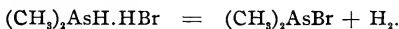
The bottle containing the bulb of arsine was surrounded by a freezing mixture (-10°) and dry carbon dioxide was passed through the apparatus until the air was displaced. After breaking the arsine bulb by means of a glass rod inserted through the cork of the bottle, a stream of pure, dry hydrobromic acid was passed through the apparatus. Absorption in the arsine was noticeable, although unchanged arsine and hydrobromic acid contributed a steady stream of outgoing gas, which was completely soluble in the wash bottles containing the potassium hydroxide and silver nitrate solutions. After some time the bottle containing the reaction mixture was detached and was found to have increased largely in weight, though, of course, not quantitatively, according to the equation



In another experiment the bottle containing the arsine was not detached, but the freezing mixture was removed and the contents of the bottle were permitted to warm to the room temperature. A marked change took place in the composition of the gas evolved; only a little arsine, but much hydrogen was collected. The latter was identified in the usual manner. The liquid remaining in the bottle was dissolved in water, treated with hydrogen sulphide and was proved to be cacodyl

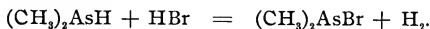
¹ Ann. Chem. (Liebig), 321, 161.

bromide. Therefore, at -10° to 20° , *dimethylarsine hydrobromide* is decomposed as follows :



Aqueous Hydrobromic Acid and Dimethylarsine.

When 1.95 grams of dimethylarsine (1 mol.) were treated, in a sealed tube, with 4 grams of a 45 per cent solution of hydrobromic acid (excess of 1 mol.) no reaction was observed even after standing for 2 months ; the arsine remained undissolved as an upper layer. Upon opening the tube in connection with a Hempel burette, no gas was given off, but it was found that the contents of the tube fumed in the presence of air. The same conditions were observed even after heating to 95° for 1 hour ; but after heating to 125° for 24 hours a quantity of hydrogen equal to more than one-half of the hydrogen in the original 1.95 grams of arsine was collected ; the liquid contents of the tube fumed only slightly on being exposed to the air ; by its odor and immediate precipitation with hydrogen sulphide it was easily proved to contain cacodyl bromide. Thus the reaction with a solution of hydrobromic acid, at an elevated temperature, is as follows :



Dry Hydriodic Acid and Dimethylarsine.

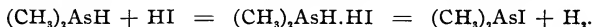
Dimethylarsine was treated with dry hydriodic acid as with dry hydrobromic acid. Their contact at room temperature was attended by an evolution of heat and the formation of a white, crystalline mass, which soon began to effervesce and to be transformed into a light yellow liquid, this, by its odor and immediate precipitation from an aqueous solution by hydrogen sulphide, was identified as cacodyl iodide. The rapidity of the decomposition of the dimethylarsine hydriodide, according to the equation



made it impossible to isolate it for study or for analysis. However, a determination was made of the amount of hydrogen evolved by a given amount of dimethylarsine :

0.6248 gram dimethylarsine gave 150.5 cc. hydrogen at 747 mm. and $25^{\circ} = 0.01175$ gram H_2 .

Theoretically, 0.648 gram of dimethylarsine gives 0.01175 gram of hydrogen. Therefore, dimethylarsine was nearly quantitatively transformed into cacodyl iodide and hydrogen, by the action of hydriodic acid, according to the equation :



Parsons¹ found that arsine itself is not acted upon by halogen acids, in aqueous solutions. Janowsky and Napoli,² however, found that it reacts with dry hydrochloric acid. From consideration of the above reactions it seems very probable that both dry halogen acids and their aqueous solutions will react with arsine, at sufficiently high temperatures.

Sulphuric Acid and Dimethylarsine.

When 6.6 grams of dimethylarsine and 4.5 grams of sulphuric acid (sp. gr. 1.84) were brought into contact, in a sealed tube containing carbon dioxide, heat was produced at the planes of contact. After standing for some time the contents of the tube separated into liquid layers, a heavy white oil and a lighter liquid of a pale yellow color. Heating 3 hours increased the volume of the lower layer.

Large, colorless, prismatic crystals slowly formed in the lower layer, the whole of which became solid at -16° . Some of these crystals were removed, dried on a clay plate over sulphuric acid, and analyzed :

0.0979 gram substance gave 0.0706 gram $BaSO_4$.

S	Calculated for	Found.
	$[(CH_3)_2AsH]_2H_2SO_4$	
	10.32	9.90

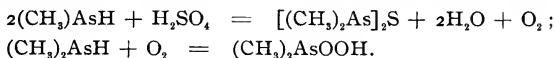
Dimethylarsonium sulphate decomposes slowly in air, and rapidly in water, forming sulphuric acid and arsine.

Cacodylic acid proved to be present in the lower layer of the reaction products. By adding water to a portion of it and boiling so as to exclude the air, all arsine passed off, leaving a clear solution that yielded the usual tests for cacodylic acid.

¹ Chem. News, 35, 236.

² Ber. d. chem. Ges., 6, 220; 8, 1637. Silf. Am. J., [2], 18, 190.

The yellow oil constituting the upper layer (3 grams) was separated and distilled. It was found to boil at 210° – 213° (cacodylic sulphide boils at 211°) and possessed the peculiar odor of cacodylic sulphide. Equations indicating the formation of cacodylic sulphide and cacodylic acid are as follows :



When dimethylarsine is passed through sulphuric acid for some time, as in the case of the sulphuric acid contained in the wash bottle beyond the condenser in the preparation of dimethylarsine, a copious precipitate of arsine trisulphide is produced. Too little data is available to explain its formation.

Sulphuric acid is reported to have no effect on arsine.¹

The Oxides of Nitrogen and Dimethylarsine.

All of the oxides of nitrogen, except nitrous oxide, attack dimethylarsine at ordinary temperatures and are reduced to nitrous oxide or nitrogen, while the arsine itself is variously oxidized, cacodylic acid being the most abundant product.

Nitrous Oxide and Dimethylarsine.

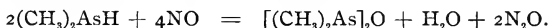
When 38.6 cc. of a mixture of hydrogen and dimethylarsine, containing 20 per cent of the latter, were treated with 41.4 cc. of nitrous oxide, no evident reaction resulted after standing 5 minutes, at the ordinary temperature. After washing with water to remove the nitrous oxide, the gas was treated with silver nitrate solution ; there resulted a precipitation of silver and a contraction equal in volume to that of the arsine present in the original mixture, therefore, nitrous oxide has no effect on dimethylarsine at ordinary temperatures.

Nitric Oxide and Dimethylarsine.

When a mixture of hydrogen and dimethylarsine was treated with an excess of nitric oxide, the resulting mixture did not fume in the air nor precipitate with silver nitrate ; therefore, the arsine was completely oxidized. When an excess of arsine was used the resulting gas did not become brown

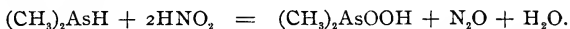
¹ Ber. d. chem. Ges., 16, 2947 ; 17, 209, 377, 674. Z. anal. Chem., 22, 147 ; 22, 148.

on mixing with air, hence, the nitric oxide was completely reduced. In both cases a clouding and an odor suggestive of cacodylic oxide were manifest. When 73.7 cc. of nitric oxide were treated in a mercury burette, with 44.6 cc. of a mixture of hydrogen and dimethylarsine, containing 20 per cent of the latter, a contraction of 15.3 cc., equal to nearly twice the volume of arsine involved, resulted. All of the data are best expressed by the following equation :

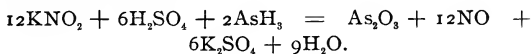


Nitrous Acid and Dimethylarsine.

When 0.79 gram of dimethylarsine (1 mol.) was treated in a sealed tube, filled with carbon dioxide, with 2 grams of potassium nitrite (4 mols.) and an excess of hydrochloric acid (6 mols.) contained in 50 cc. of water, an immediate reaction took place; heat was generated and a yellow-white opacity was imparted to the solution. On opening the tube 99.8 cc. of gas were collected and analyzed; it yielded 26 per cent of carbon dioxide, 11 per cent of unchanged arsine and 63 per cent of a gas which gave a good test for nitrous oxide, but may also have contained free nitrogen. The aqueous solution in the tube was proved to contain unchanged dimethylarsine, cacodyl, cacodylic acid and a little cacodylic chloride. Evidently the main reaction was :



When Parsons¹ treated arsine with nitrous acid he obtained the following reaction :

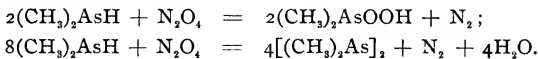


Nitrogen Tetroxide and Dimethylarsine.

Dimethylarsine and liquid nitrogen tetroxide, in equal molecular proportions, contained in small bulbs, were sealed in a tube filled with carbon dioxide. The dimethylarsine bulb was first broken and then the tip of the capillary of the nitrogen tetroxide bulb, so that the oxide distilled slowly into the

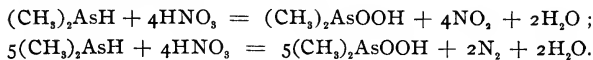
¹ Chem. News, 35, 235.

vapors of the dimethylarsine. An intense flame-reaction resulted and sufficient heat was liberated to melt the sealed tube at the point of the reaction. A black metallic deposit, a white solid, and a little liquid resulted. On opening the tube great pressure was observed; the gas was proved to contain nitrogen, but none of its lower oxides. Unchanged arsine, cacodyl, cacodylic acid (0.3 gram acid—theory 2.3 grams) and the black polymer were identified as the oxidation products. The last-mentioned compound probably results from the heat (cf. p. 9) of the following reactions:



Action of Nitric Acid on Dimethylarsine.

When 0.83 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 1.4 grams of nitric acid (2 mols.), contained in 30 cc. of water, no evident reaction was manifest, even after heating for 1 hour, at 125°. However, when 0.69 gram of dimethylarsine (1 mol.) and 5 cc. of concentrated nitric acid (23 mols.) were brought together in a sealed tube, filled with carbon dioxide, an energetic reaction resulted; red and black polymers were formed, while a flame and much heat were produced. The gaseous contents of the tube were colored brown by the presence of nitrogen peroxide; 82.1 cc. were collected and washed with water (loss 8.9 cc.), then with potassium hydroxide (loss 22.5 cc.); the residual gas proved to be nitrogen. The liquid contents of the tube were found to contain arsenic acid, cacodylic acid, and a little gray substance which was insoluble in water and nitric acid. Here, as with nitrogen tetroxide, the formation of the polymers may be due to the heat of the reactions:



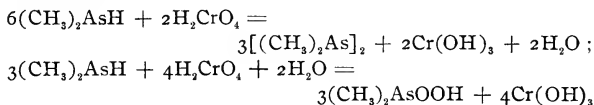
Evidently other reactions are necessary to account for the arsenic acid and the insoluble substance.¹

¹ Cf. Primary Arsines. *THIS JOURNAL*, 33, 125, 144.

Chromic Acid and Dimethylarsine.

An aqueous solution of 1 gram (4 mols.) of chromic anhydride was treated, in a sealed tube, with 0.91 gram of dimethylarsine (3 mols.). An immediate reaction was observed, the yellow of the chromic acid solution being changed gradually, during 24 hours, to a deep yellow solution and there being precipitated a dirty green solid, with a few heavy, oily drops. After 2 months the tube was opened; the gaseous portion and the oily drops were found to fume. This fuming, its odor and boiling point, proved the oil to be cacodyl and not unchanged arsine. The dirty green precipitate was washed successively, with water, alcohol and ether, then dried at 100° and identified, by its loss in weight, as chromium hydroxide. By ignition 0.0437 gram gave 0.0323 gram or a loss of 26 per cent. Chromium hydroxide loses 26.09 per cent.

The green solution was filtered, treated with an excess of ammonia, boiled and filtered free from chromium hydroxide. After evaporating on the water-bath crystals of cacodylic acid were found. Therefore, dimethylarsine is oxidized by chromic acid as follows:



It will be observed that an excess of chromic acid is favorable to the formation of cacodylic acid, while small quantities of chromic acid oxidize the arsine to the cacodyl stage only.

Parsons reports that chromic acid has no effect on arsine itself.¹

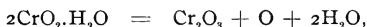
Potassium Bichromate and Dimethylarsine.

When a mixture of dimethylarsine and hydrogen is treated in a Hempel burette, with excess of an aqueous solution of potassium bichromate, a loss in volume equal to the arsine present is produced. For instance, when such a gaseous mixture, known to contain 21.7 per cent of arsine, was treated in this

¹ Chem. News, 35, 236.

manner, two determinations gave losses of 21.5 per cent and 21.7 per cent, respectively. When the arsine comes into contact with the potassium bichromate, an immediate darkening of the latter is observed and there is precipitated an amorphous solid of a brown-red color. When 0.67 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 3 grams of potassium bichromate (nearly 2 mols.) an immediate brown-black darkening of the solution was observed. Upon opening the tube the odor of arsine had disappeared. The brown-red precipitate was filtered, washed and dried at 100°. Upon igniting, 0.0301 gram of this solid and 0.0223 gram of a dark green solid resulted.

According to the equation¹



there should result 0.0222 gram of chromium trioxide.

Molybdic Acid and Dimethylarsine.

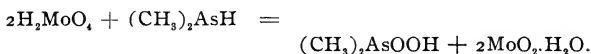
When 2.13 grams of dimethylarsine (1 mol.) were treated, in a sealed tube, with 6 grams of molybdic acid (2 mols.) and 25 cc. of water, a slow reaction was noticed—the white, insoluble acid gradually, during 1–7 days, changed through slate, green-white and blue, to a blue-black color. On opening the tube no odor of arsine was detected; the clear, aqueous solution gave, by evaporation, well formed crystals of cacodylic acid. The precipitate, when wet by liquids, possessed a beautiful, iridescent, royal-purple hue, but when dry was blue-black in color. It was washed by decantation, first with water, then with concentrated ammonia, to extract the unchanged molybdic acid. The residue, blue-black in color and insoluble in ammonia, was dried at 100° and ignited to a dull red heat. It was found to lose weight, change to the white or light yellow of molybdic acid, and become easily soluble in ammonia. On igniting 0.5410 gram of the solid, 0.5148 gram resulted; according to the equation



there should result 0.5148 gram, therefore, the blue-black

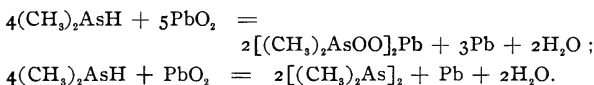
¹ Ann. Chim. Phys., [5], 21, 199.

solid was hydrated molybdenum dioxide and the reaction of molybdic acid with dimethylarsine was :



Lead Peroxide and Dimethylarsine.

When 0.66 gram of dimethylarsine (1 mol.), 15 grams of lead peroxide (1 mol.) and 50 cc. of water were brought into contact, in a sealed tube, a slow reaction was noticed ; the peroxide was gradually replaced by a metallic mirror and granular particles of lead, while the water was rendered opaque by a white, amorphous precipitate. After a number of days the tube was opened and its contents were found to fume and to give off an odor suggestive of cacodyl rather than that of unchanged arsine. The metallic particles were easily identified as lead ; the aqueous solution was proved to contain cacodylic acid. On standing, or treating with carbon dioxide, the aqueous solution was found to deposit a more voluminous precipitate,¹ therefore, lead cacodylate was in solution and the reactions of lead peroxide with dimethylarsine are as follows :

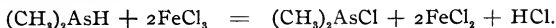


Anhydrous Ferric Chloride and Dimethylarsine.

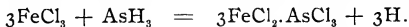
When 3.1 grams of anhydrous ferric chloride (2 mols.) in ether solution, were treated, in a sealed tube, with 1.2 grams of dimethylarsine (excess 1 mol.) there resulted an immediate voluminous precipitate of ferrous chloride ; on being filtered from the ether solution and washed with ether, then with water, it gave Turnbull's blue with potassium ferricyanide, but no pink coloration with potassium thiocyanate. The ether solution had the odor of cacodyl chloride, which was

¹ Cacodylic acid dissolves lead peroxide or lead hydroxide but not metallic lead or lead carbonate. A neutral solution of lead hydroxide in cacodylic acid gives a white amorphous precipitate on being treated with carbon dioxide.

identified as such by treatment with hydrogen sulphide. The reaction was as follows :

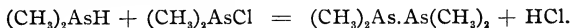


Napoli concludes¹ that the action of ferric chloride on arsine is



Cacodyl Chloride and Dimethylarsine.

When molecular quantities of dimethylarsine and cacodyl chloride were mixed in a sealed tube and heated 2-3 hours, at 100°, an oil, less mobile than the original substances, was obtained. On cooling to -20° the oil crystallized in large, beautiful, white crystals ; it was identified as cacodyl by its melting point, its boiling point and its inflammability in air. As hydrochloric acid was detected on opening the tube, the following equation is justified :



Platinic Chloride and Dimethylarsine.

A bulb containing 0.8 gram of dimethylarsine and 20 drops of a 10 per cent solution of platinic chloride were sealed in a tube filled with carbon dioxide. The capillary of the bulb was broken so that the arsine distilled slowly into the tube ; a brown-red precipitate was first formed, but it finally gave way to a bright yellow one. The tube was heated an hour, at 130° ; on cooling, complete solution of the precipitate and a heavy oil were noticed. On opening the tube an increase of 56.8 cc. of gas was observed ; after freeing from carbon dioxide and unchanged dimethylarsine, the residue, 28.8 cc., proved to be hydrogen.

Another tube, prepared as above and kept at the room temperature for a number of days, also yielded hydrogen, but the yellow solid remained largely undissolved.

After freeing the tube from the excess of dimethylarsine by exhausting with the pump, the contents, a heavy oil possessing fuming properties, proved to be cacodyl. After the latter was oxidized cacodyl chloride was detected by its odor and its precipitation with hydrogen sulphide.

¹ J. prakt. Chem., 64, 93.

When 0.59 gram of dimethylarsine (2 mols.) was treated with 4 cc. of a 10 per cent solution of platinic chloride (1 mol.) and the solution was evaporated nearly to dryness, light yellow, compact crystals were obtained. They were washed, dried and analyzed :

0.028 gram substance, dried at 110° , gave 0.0084 gram Pt.

Crystals from another sample were analyzed :

0.1048 gram substance gave 0.0348 gram Pt.

	Calculated for [(CH ₃) ₂ AsH] ₂ H ₂ PtCl ₆ .	I.	Found. II.
Pt	31.57	30.00	33.20

Evidently the substances formed were not homogeneous ; this conclusion is confirmed by the following experiments :

When gaseous dimethylarsine was passed through a 10 per cent solution of platinic chloride, at ordinary temperatures, so that the latter was always present in excess, no hydrogen was formed, but a copious, dark brown precipitate. It was washed with water, alcohol and ether, then dried and analyzed :

0.0639 gram substance, dried in vacuum desiccator, gave 0.0248 gram Pt = 38.81 per cent.

0.0839 gram substance, dried at 78° , gave 0.0345 gram Pt = 41.12 per cent.

0.2362 gram substance, dried at 100° , gave 0.0990 gram Pt = 41.91 per cent.

0.0819 gram substance, dried at 110° , gave 0.0345 gram Pt = 42.12 per cent.

0.0854 gram substance, dried at 120° , gave 0.0360 gram Pt = 42.15 per cent.

0.1738 gram substance, dried at 130° , gave 0.0759 gram Pt = 43.65 per cent.

Theory for (CH₃)₂AsHH₂PtCl₆ = 38.10 per cent.

Theory for (CH₃)₂AsClPtCl₄ = 41.12 per cent.

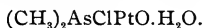
Evidently, when platinic chloride is present in excess, 1 molecule of dimethylarsine unites with 1 molecule of platinic acid and, as seen above, when the dimethylarsine is present in excess, 2 molecules of it unite with 1 of platinic acid. The

formation of hydrogen and of $(\text{CH}_3)_2\text{AsClPtCl}_4$ can be expressed by the equation



However, the above data and studies are too limited to draw definite conclusions, either as to the composition of the various precipitates or as to their decompositions.

Bunsen describes¹ a platinic chloride salt of cacodyl chloride that agrees in composition with the formula



He obtained a red-brown precipitate and recrystallized it from hot water, by which it was changed to colorless needles; we obtained the red-brown substance by his method and dried it in vacuum, when it gave the following results on analysis:

0.125 gram substance gave 0.0312 gram Pt = 24.96 per cent.

At 70° this red-brown substance gave off fumes of cacodyl chloride and changed to a lemon-yellow color. It was heated to constant weight and analyzed:

0.1240 gram substance gave 0.0487 gram Pt = 38.54 per cent, a value that agrees closely with Bunsen's (38.34) and with the theory of the substance he describes (38.48). Evidently this compound, like the platinic chloride salts of dimethylarsine, decomposes even by mild heating and, as was determined by experiment, varies largely in composition according to the method of preparation.

Soubeiran² and Simon³ claimed that arsine precipitated metallic platinum from platinic chloride solutions; Napoli⁴ gives the following equation:



while Tivoli⁵ holds that the composition of the precipitate is HAsPtO . A closer study of the platinum and other salts of the arsines will be made during the year.

¹ *Jahres. d. Chem.*, **21**, 500.

² *Ann. Chim. Phys.*, **43**, 407.

³ *Pogg. Ann.*, **42**, 563. *Jahres. d. Chem.*, 1839, p. 138.

⁴ *J. prakt. Chem.*, **64**, 93.

⁵ *Gazz. chim. ital.*, **14**, 487. *Jahres. d. Chem.*, 1884, p. 459.

Auric Chloride and Dimethylarsine.

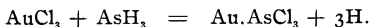
When an excess of dimethylarsine (8 mols.) was treated, in a sealed tube, with an aqueous solution of gold chloride, an immediate precipitation and decolorization of the solution resulted. The first contact of the arsine with the solution gave rise to a light yellow, flocculent precipitate that was replaced, on mixing thoroughly, by a brown-black precipitate and a few golden flakes. The tube was opened and the excess of arsine was removed by heating on the water-bath and exhausting with the pump. The precipitate was washed with water, alcohol and ether and dried at 110°. Samples from two different experiments were analyzed :

0.0345 gram substance gave 0.0377 gram gold = 93.62 per cent.

0.0499 gram substance gave 0.0488 gram gold = 97.77 per cent.

The solution contained cacodyl, cacodyl chloride and cacodylic acid.

Napoli¹ considers the action of gold chloride on arsine to be as follows :

*Silver Nitrate and Dimethylarsine.*

When gaseous dimethylarsine is treated with an excess of silver nitrate solution, the former is completely absorbed and the latter suffers a precipitation of a silver-like mirror or a gray-black, granular solid. When a mixture of dimethylarsine and an inert gas, such as hydrogen, is shaken with silver nitrate solution, it loses its arsine completely, as is shown by the loss of its fuming property when treated with air and also by the loss of its odor.

When 0.074 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 1.2 grams of silver nitrate (1 mol.), dissolved in 24 cc. of water, an immediate reaction took place ; heat was evolved, the inner walls of the tube were coated with a silver mirror, and a large quantity of the black, granular

¹ J. prakt. Chem., 64, 93.

precipitate was formed. After washing with water, alcohol and ether, and drying at 95° ,

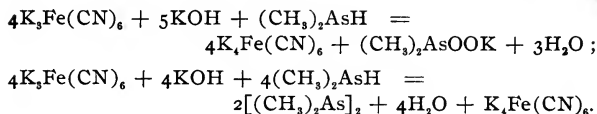
0.4380 gram substance gave 0.5658 gram of $\text{AgCl} = 97.29$ per cent Ag.

Though largely composed of silver, in this case, evidently, other products are formed.

For the various opinions of the reactions of arsine with silver nitrate, consult Gmelin-Kraut's "Handbuch der Chemie."

Potassium Ferricyanide and Dimethylarsine.

When 0.93 gram of dimethylarsine (1 mol.) was treated with an aqueous solution of 10 grams of potassium ferricyanide (less than 4 mols.) and 2 grams of potassium hydroxide (less than 5 mols.), an immediate change of color to the yellow of potassium ferrocyanide resulted. In the reaction product potassium ferrocyanide, cacodyl and potassium cacodylate were identified. No potassium ferricyanide was found. Therefore, the reaction was quantitative according to the equations:

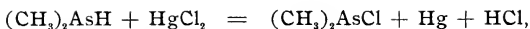


Parsons¹ concludes that none of the cyanic acids affect arsine.

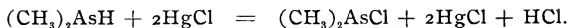
Mercuric Chloride and Dimethylarsine.

When 1 molecule of mercuric chloride, in ether solution, was treated in a sealed tube, with a slight excess of 1 molecule of dimethylarsine, a flocculent, white precipitate was formed, but soon disappeared with the production of metallic mercury. On opening the tube, the ether solution was evaporated; the residue contained no mercury and possessed the odor of cacodyl chloride, which was further identified by the hydrogen sulphide test. Therefore, the dimethylarsine reduced the mercuric chloride, quantitatively, to metallic mercury, according to the equation

¹ Chem. News, 35, 236.



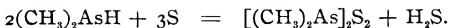
with the probable intermediate reaction¹



Sulphur and Dimethylarsine.

Sulphur reacts readily with dimethylarsine, forming different sulphides according to the quantity of sulphur used.

When 1.278 grams of dimethylarsine (2 mols.) were treated, in a sealed tube, with 0.8 gram of flowers of sulphur (excess 3 atoms) a gradual solution of the sulphur was noticed and the reaction was complete in 24 hours, at ordinary temperatures, the sulphur having changed to a white, crystalline solid. On opening the tube there was observed no arsine, but a pressure of hydrogen sulphide and a strong odor resembling asafoetida. The contents of the tube were extracted with hot alcohol, filtered, evaporated to dryness and the residue crystallized from ether. Small, granular crystals were obtained, having the characteristic odor of cacodyl sulphide. They melted at 50°, the melting point obtained by Bunsen² for cacodyl sulphide, $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$:



When sulphur is used in smaller proportions, liquid cacodyl sulphide³ is formed. When 3.9 grams of dimethylarsine (2 mols.) were brought into contact with 1 gram of sulphur (less than 1 mol.), immediate reaction was shown by the evolution of heat; the solution was complete after standing 2-3 days. On opening the tube hydrogen sulphide, but no arsine, was given off. On distilling the liquid content of the tube it was found to boil mostly at 211°; the last fraction, boiling at 211°-220°, deposited crystals in the tube of the condenser; a residual red oil was identified as arsine trisulphide. The fraction boiling at 211° was analyzed:

0.1526 gram liquid gave 0.1428 gram BaSO_4 .

¹ Cf. Primary Arsines. *THIS JOURNAL*, **33**, 127. For the reactions of arsine with mercuric chloride, *vide* *Ann. Chim. Phys.*, **33**, 355. *Pogg. Ann.*, **9**, 308; **51**, 423. *Compt. rend.*, **79**, 118. *Chem. News*, **34**, 167. *Jahres. d. Chem.*, **21**, 112.

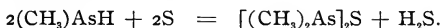
² *Ann. Chem. (Liebig)*, **46**, 16.

³ *Ibid.*, **37**, 16.

S	Calculated for [(CH ₃) ₂ As] ₂ S.	Found.
	13.22	13.15

On standing in contact with air, the oil formed a white, crystalline solid consisting of cacodylic acid and cacodyl disulphide. This is in accordance with the properties of cacody monosulphide as described by Bunsen.

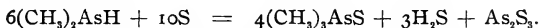
Therefore, the reaction of dimethylarsine with a small quantity of sulphur, is as follows :



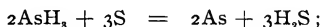
The above mentioned crystals, formed in the tube of the condenser, were pure white, glistening needles that were soluble in chloroform, carbon bisulphide and alcohol, but were insoluble in ether. They melted at 177°.5 and had a peculiar mercaptan-like odor.

S	Calculated for (CH ₃) ₃ AsS.	Found.
	21.05	21.31

Their formation may be expressed by the equation :



The reactions of arsine with sulphur are reported to be as follows:¹



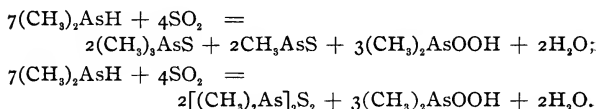
Sulphur Dioxide and Dimethylarsine.

When 2.17 grams of dimethylarsine (1 mol.) and 1.5 grams of liquid sulphur dioxide (excess of 1 mol.) were brought together in a sealed tube, immediate reaction took place; much heat was liberated and an orange-colored liquid was formed which, on standing, changed almost entirely to a white, crystalline solid. On opening the tube there was observed a slight pressure of a gas which contained no sulphur dioxide, hydrogen sulphide, or dimethylarsine, but which had the odor of asafœtida.

The small quantity of liquid was poured from the tube into

¹ Gmelin-Kraut : " Handbuch der Chemie."

a beaker, when it immediately began to deposit crystals which were found to melt at 50° , the melting-point of cacodyl disulphide. The crystalline solid in the tube was dissolved in hot alcohol and its solution evaporated to dryness on the water-bath; it gave a residue difficultly soluble in ether. The first ether extract gave white needles which melted at 165° – 170° , $(\text{CH}_3)_3\text{AsS}$ melts at 170° . The second ether extract gave another crystalline solid which melted at 110° ; CH_3AsS melts at that temperature.¹ The solid, left after extracting the ether, was found to contain cacodylic acid. Therefore, it is evident that cacodyl disulphide, methylarsine sulphide, trimethylarsine sulphide and cacodylic acid are products of the action of liquid sulphur dioxide on dimethylarsine. The reactions are represented by the equations:



Disulphur Dichloride and Dimethylarsine.

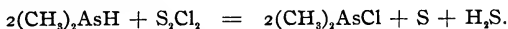
It was found by Michaelis and Luxenbourgh² that when disulphur dichloride acted upon dimethylamine, an oil, dithiodimethylamine, $[(\text{CH}_3)_2\text{N}]_2\text{S}_2$, was formed. It was expected that treatment of dimethylarsine with the same reagent would give dithiodimethylarsine or cacodyl disulphide; but it was found that the reaction proceeds further, disulphur dichloride acting as a chlorinating agent, formed cacodyl chloride and deposited free sulphur.

When 2 molecular proportions (1.9 grams) of dimethylarsine were mixed carefully with 1 of disulphur dichloride (1.2 grams) much heat was evolved and a yellow solid separated from the reaction-mixture. On opening the tube hydrogen sulphide was observed. The contents of the tube were extracted with ether and the ether solution was evaporated. The residue, smelling strongly of cacodyl chloride, was dissolved in water and identified by its immediate precipitation with hydrogen sulphide.

¹ Ann. Chem. (Liebig), 107, 269.

² Ber. d. chem. Ges., 28, 166.

The yellow solid, insoluble in ether, melted at $114^{\circ}.5$; rhombic sulphur melts at that temperature. Therefore, the above reaction was as follows:



Stannic Chloride and Dimethylarsine.

When stannic chloride reacts with dimethylarsine a reduction to metallic tin does not take place, but hydrochloric acid is eliminated and the compound *dimethylarsine chlorstannide*, $(\text{CH}_3)_2\text{As}.\text{SnCl}_3$, is formed. This reaction is analogous to the formation of $(\text{C}_2\text{H}_5)_2\text{N}.\text{SiCl}_3$, $(\text{C}_2\text{H}_5)_2\text{N}.\text{BCl}_2$, etc., from dimethylamine.¹

When 2 grams of dimethylarsine (1 mol.) and 4.9 grams of stannic chloride (1 mol.) were brought into contact, in a sealed tube, they reacted violently with a flame and the liberation of much heat, a white, crystalline solid being produced. When one end of the tube was heated at 100° , the solid sublimed to the cooler part, where it formed large, beautiful, colorless needles, some attaining the length of 2 cm. Dimethylarsine chlorstannide is quite stable in dry air, but is liquefied slowly by moist air. It has a very penetrating and disagreeable odor. It is easily soluble in ether and carbon bisulphide, but less so in chloroform.

I. 0.0314 gram substance required 0.0479 gram AgNO_3 .

II. 0.1674 gram substance required 0.2559 gram AgNO_3 .

	Calculated for $(\text{CH}_3)_2\text{As}.\text{SnCl}_3$.	I.	Found.	II.
Cl	32.22	31.91		31.80

Phosphorus Trichloride and Dimethylarsine.

When phosphorus trichloride (5.5 grams) reacted, in a sealed tube, with 1 molecular proportion of dimethylarsine (5 grams) heat was evolved and an orange-yellow solid was precipitated.

On opening the tube a pressure of hydrochloric acid and an odor of cacodyl chloride were observed. The cacodyl chloride was identified by the boiling point (100°) and its immediate precipitation from a water solution by hydrogen sulphide.

¹ Ber. d. chem. Ges., 29, 710.

The orange solid was found to be insoluble in all ordinary organic solvents and to contain no arsenic. It was not obtained sufficiently pure for satisfactory analysis, but its high per cent of phosphorus makes it probable that it is $(\text{CH}_3\text{P})_x$, or the compound $(\text{CH}_3)_2\text{P}_4$,¹ with which it agrees in properties.

Janowsky² found that arsine and phosphorus trichloride reacted as follows :



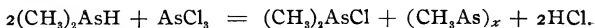
Arsenic Trichloride and Dimethylarsine.

Four and a half grams of dimethylarsine (1 mol.) and 7.8 grams of arsenic trichloride (1 mol.) reacted at ordinary temperatures, liberating heat and forming an oil and a dark brown solid. The reaction products were extracted with chloroform and the chloroform solution, which smelled of cacodyl chloride, was distilled. After the chloroform had been removed the temperature rose to 100° – 104° ; the distillate was identified as cacodyl chloride. After washing with chloroform, alcohol and ether and drying at 110° , the brown, amorphous solid was analyzed :

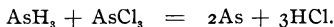
0.4089 gram substance gave 0.7116 gram $\text{Mg}_2\text{P}_2\text{O}_7$.

	Calculated for $(\text{CH}_3\text{As})_x$.	Found.
As	83.33	84.25

The substance was probably the polymer $(\text{CH}_3\text{As})_x$ and some free arsenic. The equation representing the reaction is, perhaps,



Janowsky³ found that arsine and arsenic trichloride reacted as follows :



Antimony Trichloride and Dimethylarsine.

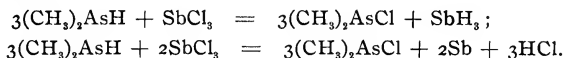
Dimethylarsine (3.8 grams) was brought into contact, in a sealed tube, with 1 molecular proportion of antimony trichloride.

¹ Ann. Chem. (Liebig), 104, 4.

² Ber. d. chem. Ges., 6, 216.

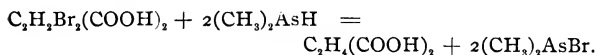
Ibid., 6, 219.

ide (8 grams) ; a heavy, transparent oil and a black, metallic deposit resulted. After heating 5 hours, at 100° , considerable pressure was observed ; on opening the tube a gas (stibine), which gave an antimony mirror, was evolved. The black deposit was separated from the oil by means of ether and hydrochloric acid and identified as metallic antimony. Cacodyl chloride was easily recognized in the reaction products, by its odor and its precipitation as cacodyl sulphide. The heavy oil decomposed at ordinary temperatures, giving off a gas and depositing metallic antimony. It was probably an intermediate product of the action. The reactions, at least in part, are as follows :



Dibromsuccinic Acid and Dimethylarsine.

When dibromsuccinic acid (2 grams) was treated, in a sealed tube, with 1.5 grams of dimethylarsine (2 mols.) there was an immediate precipitation of a white, crystalline solid. No pressure was observed on opening the tube. After washing with ether and recrystallizing from water, the crystals melted at 185° and gave no test for bromine or arsenic. Therefore, they were succinic acid, which melts at 185° . Cacodyl bromide was identified in the ether solution. The reaction was

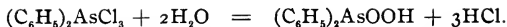


Aromatic Secondary Arsines.

These arsines, like the aliphatic secondary arsines, can be prepared by reducing the corresponding arsinic acids, no difference in the ease of their reductions being noticeable.

Diphenylarsinic acid, $(\text{C}_6\text{H}_5)_2\text{AsOOH}$, was chosen for reduction because of the ease with which it can now be prepared and purified. It was first obtained by Michaelis and La Coste¹ from diphenylarsine trichloride, the transformation being quantitative, according to the equation :

¹ Ann. Chem. (Liebig), 201, 231.

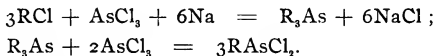


The trichloride is formed by chlorinating diphenylarsine chloride,

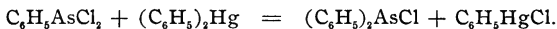


Having the monochloride, it is only necessary, therefore, to cover it with water, saturate with chlorine or bromine, and to warm, when complete transformation to the diphenylarsinic acid results, according to the two equations mentioned above. The only difficulty hitherto involved has been the preparation of pure diphenylarsine chloride. It has been produced, up to the present, by the application of Michaelis' general method for the formation of secondary aromatic compounds.¹

The triphenylarsine is first obtained by condensing the aliphyl monohalide and arsenic trichloride by means of sodium and is subsequently heated at 250°, in a sealed tube, with 4-5 parts of arsenic trichloride, for 30 hours.² The transformations are nearly quantitative, as follows:



Monophenylarsine chloride thus obtained is then phenylated by heating to 255°, with less than 0.5 molecular quantity of mercury phenyl,³ the reaction being, of course, far from quantitative, according to the equation:



The mixture of mono- and diphenylarsine chlorides thus obtained is separable only by a laborious process of fractional distillation. By employing the following method, the preparation and use of mercury phenyl is dispensed with, a single process of dephenylation is substituted for both the dephenylation and the subsequent phenylation, and an admixture of diphenylarsine chloride with the mono- or the triphenyl arsenic compounds does not involve difficulties of separation.

¹ Ann. Chem. (Liebig), **201**, 215.

² Ber. d. chem. Ges., **27**, 263.

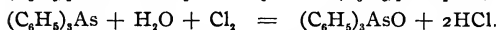
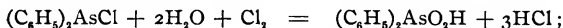
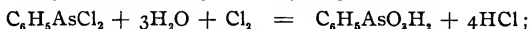
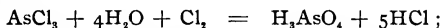
³ Ann. Chem. (Liebig), **207**, 115.

Preparation of Diphenylarsinic Acid.

A mixture of 360 grams of triphenylarsine¹ (2 mols.) and 300 grams of arsenic trichloride (1 mol.) was heated at 220°, in sealed tubes, for 40 hours. The dark colored reaction product was then subjected to vacuum distillation, so as to separate arsenic trichloride, phenylarsine dichloride, diphenylarsine chloride, and triphenylarsine from one another as sharply as possible and to observe better the course of the dephenylation. For the preparation of phenylarsonic acid or diphenylarsinic acid from this mixture ordinary distillation will suffice, or it may be entirely dispensed with. The lowest fraction, boiling as high as 150° (23 mm.), was washed with a little water and extracted with ether, so as to free it from arsenic trichloride; on redistilling, 148 grams (19 per cent of the theory) of phenylarsine dichloride were obtained, boiling at 139° (23 mm.). The higher fractions yielded 163 grams (38 per cent of the theory) of diphenylarsine chloride, boiling at 210° (34 mm.).

It is impossible, or at least inconvenient and unnecessary, to obtain by distillation pure diphenylarsine chloride; the pure phenylcacodylic acid may be separated from adhering compounds by an application of the method of analysis (*c*) (*vide* p. 7).

For instance, suppose there are present in a mixture the following four substances—arsenic trichloride, phenylarsine dichloride, diphenylarsine chloride and triphenylarsine. On covering with water, treating with chlorine to the point of saturation, and then boiling, the following reactions take place:

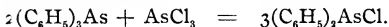


The triphenyl arsenic compounds of the last equation are insoluble in water, therefore, after filtering, only the products of the first three reactions are in solution. On treating this

¹ Ann. Chem. (Liebig), 233, 62.

solution with magnesia mixture, in the cold, the arsenic acid is, of course, quantitatively precipitated; on treating this filtrate with an excess of magnesia mixture and boiling, the magnesium salt of phenylarsonic acid is precipitated; finally, on acidifying with hydrochloric acid, diphenylarsinic acid is almost quantitatively precipitated; 100 cc. of its saturated, aqueous solution, at 27°, contains only 0.028 gram of the acid.

In short, to prepare diphenylarsinic acid, heat to 220°, for 30 hours, a mixture of triphenylarsine and arsenic trichloride, in the proportions indicated by the equation



When cool, pour into water and saturate with chlorine; filter and treat with an excess of magnesia mixture, boil and filter. On acidifying with hydrochloric acid, the diphenylarsinic acid separates first as an oil, then solidifies in beautiful, white needles. After recrystallizing once from water the acid was obtained pure. Analysis:

0.1646 gram substance gave 0.3234 gram CO_2 and 0.0602 gram H_2O .

	Calculated for $(\text{C}_6\text{H}_5)_2\text{AsO}_2\text{H}$.	Found.
C	54.96	54.78
H	4.20	4.06

The yield of the acid exceeded 40 per cent. Should it seem desirable, the phenylarsine dichloride may be separated as mentioned above and be converted into diphenylarsine chloride, the yield of diphenylarsinic acid may thus be raised to nearly 60 per cent; by the method of Michaelis¹ the yield did not exceed 18 per cent.

Since triphenylarsine and other triarylarsines react with an excess of arsenic trichloride (8–10 mols.) to form the mono-aryl compounds² and, as shown above, 2 molecules of the tertiary arsine react, largely, with 1 molecule of arsenic trichloride so as to form the secondary compound; finally, as was shown in an experiment, triphenylarsine reacts with

¹ Ber. d. chem. Ges., **27**, 264. Ann. Chem. (Liebig), **207**, 115.

² Michaelis: Ann. Chem. (Liebig), **320**, 272.

phenylarsine dichloride, when heated for 24 hours, at 240° , so as to form a large quantity of the secondary arsenic compound—it may be concluded that the proportions of the products formed at elevated temperatures depend largely upon mass influence. An effort to prepare diphenylarsine chloride by the application of this influence to the sodium condensation failed, the expected reaction :

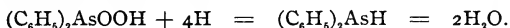


did not take place, only triphenylarsine being obtained. Benzyl chloride¹ and isoamyl chloride (*vide* p. 49), however, react, in the proportions of the above equation, giving large quantities of secondary arsine chlorides.

A discussion of the mechanism of these and other arsenic reactions will be given in a future paper.

Diphenylarsine.

This arsine, the analogue of diphenylamine, is prepared from diphenylarsinic acid :



in a manner nearly identical with that of the preparation of phenylarsine.² A quantity of the pure acid was mixed with an excess of amalgamated zinc dust and then covered with a layer of ether. The flask was connected with a reflux condenser, at the top of which was inserted a rubber stopper carrying a dropping funnel and a tube bent down into mercury ; the latter permits the exit of free hydrogen, but prevents the entrance of air.

Concentrated hydrochloric acid was placed in the dropping funnel and 5–20 cc. of it were admitted to the flask, occasionally, during 2 or 3 days, or until the completion of the reduction was assured.

During the reduction occasional energetic agitation of the flask is necessary, for two reasons : First, the arsine is soluble in ether but not in water (the diphenylarsinic acid is just the reverse) and, as it forms, it coats the zinc in contact with

¹ Ann. Chem. (Liebig), **233**, 62.

² Ber. d. chem. Ges., **34**, 3598. THIS JOURNAL, **33**, 147.

the lower aqueous layer, thus retarding the reduction process. Second, phenylcacodyl is an intermediate product of the reduction and it also coats the zinc and is dissolved, to some extent, by ether.¹ Therefore, energetic shaking, particularly at the end of the reduction, is necessary to extract the arsine and to cause complete reduction of the phenylcacodyl to diphenylarsine.

As the reduction progresses the hydrogen bubbles on the surface of the ether, become iridescent and a somewhat bluish tint is imparted to the ether solution. When the reduction is complete the solution is transferred, without contact with the air, to a separatory funnel containing some fused calcium chloride; then, after drying the ether solution, it is drawn over into a distilling flask connected with a condenser and a Brühl apparatus, which, previously, has been filled with carbon dioxide. When the apparatus is exhausted the ether may be removed and the distillation of the arsine effected. Usually so much frothing of the liquid takes place that difficulty is encountered in obtaining pure condensed vapor of the distilled substance; slow distillation, in a stream of pure carbon dioxide, gives the best results. The arsine thus obtained is a clear, colorless oil, that boils at 174° (25 mm.) and at 155° (37 mm.); from a consideration of the boiling points of its analogues and homologues,² diphenylarsine ought to boil at 250° – 260° , under ordinary pressure.

In the dilute form its odor is not so pleasant as that of phenylarsine; its more concentrated vapor produces catarrhal symptoms and sneezing. It is soluble in alcohol, ether and other organic solvents, but is insoluble in water.

0.1500 gram liquid gave 0.3387 gram CO_2 and 0.0670 gram H_2O .

	Calculated for (C_6H_5) ₂ AsH.	Found.
C	62.61	61.58
H	4.78	4.96

Oxidation of Diphenylarsine.

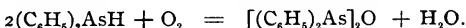
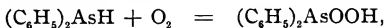
In contact with air diphenylarsine warms and changes, al-

¹ Ber. d. chem. Ges., 15, 1955.

² THIS JOURNAL, 33, 107.

most instantaneously, into a pure white or faintly yellow, hard mass; more rapid oxidation is easily discernible in the case of diphenylarsine than in that of phenylarsine. The mass was treated with excess of ammonia and warmed on the water-bath; partial solution took place. The insoluble portion was filtered, washed with water and recrystallized from ether; it was found to melt at 90° and, by its odor, was further identified as phenylcacodyl oxide.¹

When acidified, the ammonia solution yielded crystals of diphenylarsinic acid, which was identified by its melting-point and other properties.² From 1.9 grams of the oxidation product, 1.7 grams of diphenylarsinic acid and 0.2 gram of cacodyl oxide were recovered, therefore about 88 per cent of the oxidation was represented by the first and 12 per cent by the second of the following equations:



Slow oxidation is the favorable condition for the former reaction; an ether solution of the arsine, exposed to the air, precipitated only needles of diphenylarsinic acid.

Diphenylarsine and Bromine.

When 0.75 gram of diphenylarsine, in a sealed tube, was allowed to distil, slowly, into ether containing 1 gram of bromine (2 mols.) there was an immediate, voluminous precipitation of a reddish yellow solid; when the entire quantity of arsine had come into contact with the bromine, the color of the precipitate changed to a golden yellow and the crystals became compact and glistening; the ether solution was completely decolorized. On opening the tube the yellow, crystalline solid was removed, washed with ether and dried in a desiccator.

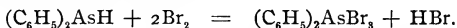
0.1656 gram substance required 0.1120 gram AgNO_3 .

	Calculated for $(\text{C}_6\text{H}_5)_2\text{AsBr}_3$.	Found.
Br	51.17	49.82

¹ Ann. Chem. (Liebig), 201, 229.

² *Ibid.*, 201, 231.

Diphenylarsine tribromide forms golden yellow plates, which soften at 120° and melt at 129° . It attacks the skin with great avidity. Water decomposes it, forming a light yellow oil, phenylcacodyl bromide. The equation for the formation of the tribromide is as follows :



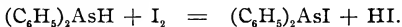
Diphenylarsine and Iodine.

When 0.9 gram of diphenylarsine (1 mol.) was treated, in a sealed tube, with 1.94 grams of iodine (less than 2 mols.) in ether solution, there resulted an immediate precipitation of a dark red oil. On opening the tube a pressure of hydriodic acid was observed. From the reaction products an oil was isolated whose analysis agreed closely with the compound, *diphenylarsine iodide*.

0.2185 gram substance gave 0.1417 gram AgI.

	Calculated for (C_6H_5) ₂ AsI.	
I	35.67	35.07

Under the above conditions diphenylarsine reacted with iodine according to the equation



Diisoamylarsine Compounds.

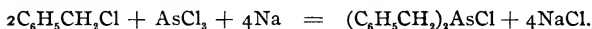
There has, hitherto, been no easy, general method for the preparation of aliphatic secondary arsenic compounds. The dry distillation of the alkali salts of fatty acids with arsenic trioxide has yielded, as yet, only secondary methyl compounds. The treatment of alkyl iodides with sodium arsenide¹ has produced secondary ethyl compounds, but no general application has been made of this reaction, largely on account of the disagreeable properties of the sodium arsenide and because its reaction with alkyl halides gives rise to mixtures of the primary, secondary and tertiary arsine derivatives which, hitherto, have been difficult to separate.

Michaelis and Paetow² found that when 2 molecular proportions of benzyl chloride were condensed, by means of sodium,

¹ Ann. Chem. (Liebig), **89**, 319.

² *Ibid.*, **233**, 62.

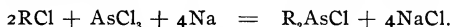
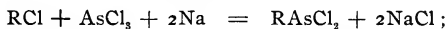
with 1 molecular proportion of arsenic trichloride, the secondary arsine compound was formed in the largest quantity, according to the equation



We have found that this reaction is applicable to the aliphatic series, for, when varied alkyl halides, such as ethyl bromide, propyl iodide and isoamyl chloride were treated in a similar manner, and their products were subjected to the same method of separation as the phenyl compounds (*vide* p. 43), solutions containing secondary arsine compounds were obtained.

In the case of isoamyl chloride, the main product was *diisoamyl chloride* or its basic compound, similar in composition to the basic cacodyl chloride obtained by Bunsen¹ and having the general formula, $6\text{R}_2\text{AsCl} \cdot (\text{R}_2\text{As})_2\text{O}$.

A quantity of liquid was obtained boiling at a temperature lower than that of diisoamylarsine chloride; it has not yet been isolated and identified, but it is probably isoamylarsine chloride, $\text{C}_5\text{H}_{11}\text{AsCl}_2$. Therefore, when alkyl halides, in general, are condensed with arsenic trichloride, by means of sodium, the mono- and dialkylarsine chlorides are formed and their relative proportions are governed by the molecular quantities of the alkyl halides and arsenic trichloride used. The general reactions are represented thus :



Diisoamylarsine Chloride.

In a 1 liter, round-bottomed flask, connected with a reflux condenser, were placed 62 grams of sodium wire (4 atoms) and 400–500 cc. of dry ether. Through a cork at the top of the condenser were inserted a dropping funnel and a glass tube, bent down into mercury, so as to prevent the entrance of air. After filling the apparatus with carbon dioxide, a mixture of 145 grams of isoamyl chloride (2 mols.) and 124 grams of arsenic trichloride (1 mol.) was added to the sodium, in small quantities at a time. The reaction was very energetic; a small por-

¹ Ann. Chem. (Liebig), 37, 49.

tion of the mixture (5 cc.) caused very violent boiling of the ether, consequently it was necessary to cool the flask by means of water. The isoamyl chloride and arsenic trichloride were added slowly, until the end of the operation; small portions, even at the end, caused quite a vigorous action. The reaction was complete in 2 hours. The ether solution was then filtered from the residue of sodium chloride and the latter was extracted several times with ether. After distilling off the ether there remained a colorless oil, which was fractionated *in vacuo*, with the following results:

Fraction.	Temperature.	Pressure. mm.	Weight. Grams.
1	140°	43	15
2	140°-148°	40-33	34
3	148°-152°	33-27	34
4	152°-160°	27-28	30
			<hr/> 115

Theory, $(C_5H_{11})_2AsCl = 172$

After one refractionation *in vacuo* and several under ordinary pressure, most of the liquid was found to boil at 263° (750 mm.). The distillation-product was a colorless oil containing, invariably, a little white, soapy precipitate.

0.1710 gram clear liquid gave 0.3036 gram CO_2 and 0.1478 gram H_2O .

	Calculated for $6(C_5H_{11})_2AsCl \cdot [(C_5H_{11})_2As]_2O$.	Found.
C	48.65	48.94
H	8.96	9.60

Basic isoamylcacodyl chloride is a colorless liquid, boiling at 263° (750 mm.) and at 148° (33 mm.). It has a peculiar and characteristic odor, not at all intense like that of cacodyl chloride. It is soluble in all the ordinary organic media, but is insoluble in water. The white, soapy solid which always separates on distilling the oil is probably *isoamylcacodylic oxide*, $[(C_5H_{11})_2As]_2O$.

In this application of the Würtz reaction to aliphatic arsenic compounds a red, amorphous solid is always formed; it is larger in quantity when the reaction is conducted in the pres-

ence of air than in its absence. In the above condensation 20 grams of this red product were obtained, while in another experiment, during which air was freely admitted, 44 grams of it were formed. The red body was decolorized by means of bromine water and yielded a yellow, crystalline solid, which was easily soluble in ammonia. From the ammoniacal solution arsenious acid, isoamylarsonic acid, and isoamylarsinic acid were obtained, in about equal quantities. The red substance is probably similar to Bunsen's "erytrarsine," $(\text{RAs})_4\text{As}_2\text{O}_3$, which would account for the isoamylarsonic acid and the arsenious acid formed by the above treatment, while an analogous dialkyl compound, $[(\text{C}_5\text{H}_{11})_2\text{As}]_4\text{As}_2\text{O}_3$, would account for the formation of the isoamylarsinic acid.

Diisoamylarsine Chlordibromide.

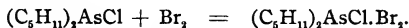
A dry, ethereal solution of diisoamylarsine chloride was treated with bromine, in ether solution, until no decolorization resulted on warming gently. The ether was evaporated and the residual oil was permitted to stand; well formed, crystalline granules separated after some time, but only to the extent of about one-third of the oil. They were filtered, washed with benzene and analyzed:

0.1412 gram substance gave 0.1868 gram $\text{AgCl} \cdot 2\text{AgBr}$, which is equal to 0.1351 gram AgBr .

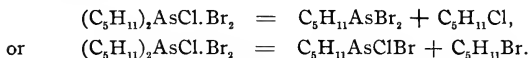
	Calculated for $(\text{C}_5\text{H}_{11})_2\text{AsCl} \cdot \text{Br}_2$.	Found.
Br	41.61	41.47

Diisoamylarsine chlordibromide is a pure white, crystalline solid which melts at 124° – 125° and has an odor resembling that of chloral hydrate. It is readily soluble in ether and chloroform, but is less so in benzene. Water dissolves it slowly, ammonia very readily, with the formation of *isoamylarsinic acid*.

The equation representing the formation of the above trihalide is as follows:

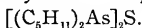


The incompleteness of this reaction is probably due to the following ones :¹



The decomposition products, being liquids and being formed to a large extent, account for the small yield of the pentavalent arsenic derivative.

Diisoamylarsine Sulphide,



When diisoamylarsine chloride is added to water and is treated with hydrogen sulphide, beautiful white needles separate at the surface of the water. When the reaction was complete, after 10 hours, the crystals were extracted with ether; the latter having been removed, an oil remained. It solidified in a freezing mixture and yielded crystals. Analysis :

0.1751 gram substance gave 0.0890 gram BaSO_4 .

	Calculated for $[(\text{C}_5\text{H}_{11})_2\text{As}]_2\text{S}.$	Found.
S	6.86	6.98

The sulphide melts at 29° – 30° , is easily soluble in ether and carbon bisulphide, difficultly soluble in alcohol and insoluble in water. The equation for its formation is as follows :



Isoamylarsinic Acid.

Isoamylarsinic acid was prepared from isoamylcacodyl chloride, by a method similar to that used for the preparation of phenylarsinic acid from phenylcacodyl chloride. Isoamylcacodyl chloride was covered with water, treated with bromine and heated until the excess of bromine was decolorized; the treatment was repeated until the bromine was no longer absorbed. By this means the oil was changed to a yellow, crystalline solid, which was found to be soluble in ammonium hydroxide. To the ammoniacal solution an excess of magnesium chloride was added in the cold, to precipitate arsenious acid; then the precipitate was boiled to precipitate the magnesium salt of isoamylarsonic acid, formed from isoamylarsine chloride

¹ Cf. Ethylcacodyl Iodide. Ann. Chem. (Liebig), 116, 367.

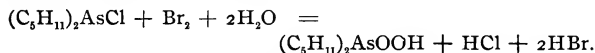
and which had not been completely removed by distillation. After filtering off the magnesium salt of the arsonic acid, the solution was made slightly acid, when the *isoamylarsinic acid* was precipitated as large, flaky crystals. After recrystallizing from water it was obtained pure.

I. 0.1132 gram substance gave 0.1175 gram CO_2 and 0.0970 gram H_2O .

II. 0.2620 gram substance gave 0.4030 gram CO_2 (H_2O was lost).

	Calculated for (C_6H_{11}) ₂ AsOOH.2H ₂ O.	I.	Found. II.
C	41.95	41.67	41.95
H	9.69	9.27	. .

Isoamylarsinic acid melts at 153° - 154° . It is easily soluble in alcohol, somewhat so in water and insoluble in ether. The equation of its formation is as follows :



Diisoamylarsine.

This arsine was prepared by the method employed for diphenylarsine, 26 grams of pure diisoamylarsinic acid being used and yielding nearly the theoretical quantity of diisoamylarsine. No difficulty was encountered in distilling the arsine, a pure product being obtained at 150° (99 mm.).

0.1347 gram substance gave 0.2715 gram CO_2 and 0.1238 gram H_2O .

	Calculated for (C_6H_{11}) ₂ AsH.	Found.
C	55.05	54.97
H	10.09	10.21

The physical properties of diisoamylarsine are quite like those of diphenylarsine; however, it has a sickening, characteristic odor, more suggestive of isoamyl alcohol than of arsine.

Oxidation Products.

On exposing diisoamylarsine to the air a more syrupy product was obtained than from diphenylarsine. On passing air

into a beaker containing 1 gram of diisoamylarsine, sufficient heat was evolved to boil some of the arsine, but no flame reaction was produced. The oxidation products were extracted, first with ammonia, then with ether. The former extract yielded diisoamylarsinic acid and the latter an oil, which was probably diisoamylcacodylic oxide.

The preparation and study of arsines, stibines and phosphines by reactions described in the preceding pages are being pursued in this laboratory.

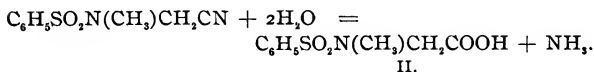
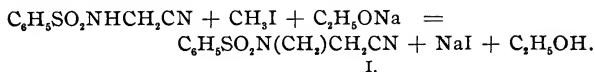
URBANA, ILL.,
July 14, 1905.

Contributions from the Sheffield Laboratory of Yale University.

CXXVIII.—SOME DERIVATIVES OF BENZENESULPHONYLAMINOACETONITRILE.

BY TREAT B. JOHNSON AND ELMER V. MCCOLLUM.

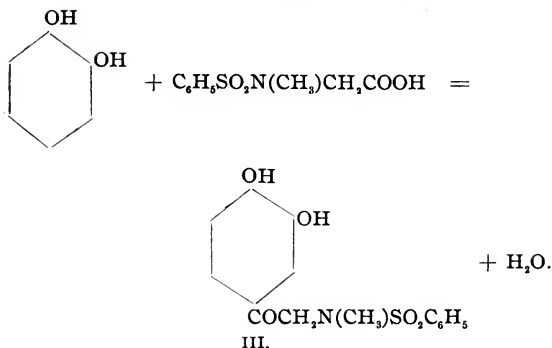
In the course of some work on the preparation of derivatives of adrenaline we had occasion to prepare benzenesulphonesarcosine. We find that this acid can easily be prepared from benzenesulphonylaminoacetonitrile.¹ When this compound was treated with methyl iodide, in presence of sodium ethylate, it was converted into benzenesulphonylmethylaminoacetonitrile (I.). This nitrile was easily hydrolyzed by hydrochloric or sulphuric acid to benzenesulphonylsarcosine (II.).



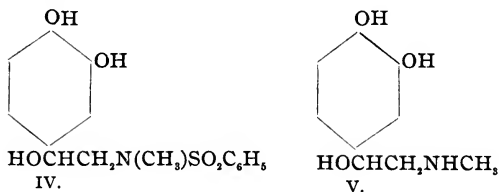
It seemed of interest to examine the behavior of this acid (II.) towards pyrocatechol. It might be expected to condense with pyrocatechol,² in presence of zinc chloride or phosphorus oxychloride, to give a benzenesulphonylmethylaminoaceto-pyrocatechol (III.):

¹ Knoevenagel and Lebach: Ber. d. chem. Ges., 37, 4094.

² Dzerzowski: Jour. der russ. chem. Ges., 25, 154. Bruhns: Ber. d. chem. Ges., 34, 92.



Such a condensation would be of special interest since, on reduction, the ketone should give a benzenesulphone derivative of adrenaline¹ (IV.) if the structure of adrenaline is to be represented as in Formula V. :²



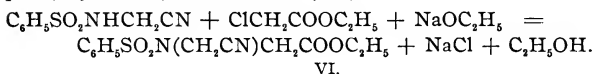
We now find that benzenesulphonesarcosine (II.) does not condense with pyrocatechol under the conditions which we employed. When we used either zinc chloride or phosphorus oxychloride as the condensing agent the only definite product isolated was unaltered acid. The same result was obtained when we attempted to condense benzenesulphonylaminoacetic acid with pyrocatechol. The acid, melting at 166°, was recovered unaltered.

¹ Fürth : Monatsh. Chem., **24**, 278 (1903).

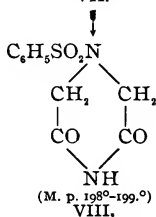
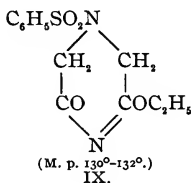
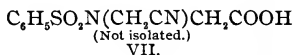
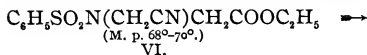
² Jowett : P. Chem. Soc., **20**, 18 (1904). Friedman : Beitr. chem. Phys. Pathol., **6**, 92 (1904). Stolz : Ber. d. chem. Ges., **37**, 4149 (1904).

In the course of our work we have prepared a series of nitriles analogous to benzenesulphonylmethylaminoacetonitrile (I.). With the exception of the ethyl and propyl derivatives they have all proved to be well crystallized compounds. In every case that we have examined they have undergone hydrolysis to the corresponding acids when warmed with hydrochloric or sulphuric acid. In the case of the lower aliphatic derivatives the hydrolysis could be effected on the steam-bath, while with the higher aromatic derivatives it was necessary to heat in sealed tubes at a high temperature.

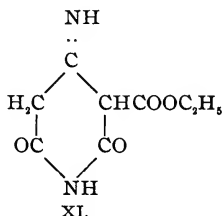
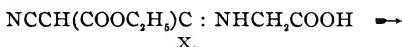
When benzenesulphonylaminoacetonitrile was treated with ethyl chloracetate, in the presence of sodium ethylate, it was converted, practically quantitatively, into ethyl benzenesulphonylcyanmethylaminoacetate (VI.):



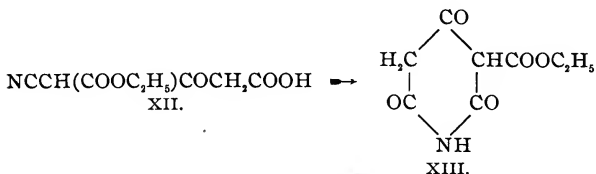
Especially interesting was the behavior of this ethyl ester (VI.) when saponified with dilute sodium hydroxide. The resulting benzenesulphonylcyanmethylacetic acid (VII.) immediately underwent a rearrangement in the alkaline solution, to an isomeric piperazine derivative (VIII.). That we were dealing here with a molecular rearrangement was established by the following experiment: When the silver salt of the product obtained by saponification (VIII.) was treated with ethyl iodide, an ethyl derivative (IX.) was obtained, which was not identical with the original ester (VI.).



This rearrangement is analogous to that of orthocyanbenzoic acid into phthalimide.¹ Two similar rearrangements have also recently been described by Thorpe² and his co-workers. They have shown that monoethyl α -cyan- β -iminoglutarate (X.) readily rearranges to α, α' -diketo- β -carbethoxy- γ -iminopiperidine (XI.) in the presence of strong sulphuric acid :



γ -Carbethoxy- γ -cyanacetoacetic acid (XII.) also underwent a similar change, when heated above its melting-point, and was transformed into 2,4,6-trioxy-3-carbethoxypyridine (XIII.) :



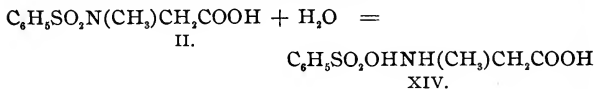
Hedin³ observed that benzenesulphonylaminoacetic acid could be boiled with hydrochloric or sulphuric acid without decomposition. We now find that the nitrogen substituted benzenesulphonylaminoacetic acids are extremely stable and can be decomposed only by very energetic hydrolysis. When benzenesulphonylmethylaminoacetic acid (II.) was boiled with

¹ Hoogewerf and Van Dorp: *Rec. Trav. Chim.*, **11**, 93.

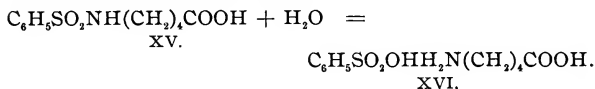
² Baron, Remfrey and Thorpe: *J. Chem. Soc.*, **85**, 1730 (1904).

³ *Ber. d. chem. Ges.*, **23**, 3196.

strong hydrochloric acid it was converted into the benzenesulphonic acid salt of sarcosine (XIV.):



This result is perfectly analogous to a previous observation by Schotten and Schlörmann.¹ They have shown that benzenesulphonylaminovalerianic acid (XV.) is hydrolyzed to the sulphonic acid salt of aminovalerianic acid (XVI.) when heated with hydrochloric acid at 180°:



E. Fischer² has shown that hippuric acid is converted into hippuryl chloride when it is dissolved in acetyl chloride and then carefully treated with phosphorus pentachloride. It seemed of interest to examine the behavior of benzenesulphonylaminoacetic acid under the same conditions. We now find that this acid reacts in an entirely different manner with phosphorus pentachloride. The benzenesulphonyl radical was removed by this treatment with the formation of benzenesulphone chloride. The acid chloride was identified by means of its anilide, which melted sharply at 110°. This remarkable result is especially interesting in view of the stability of the benzenesulphonylaminoacetic acids when warmed with hydrochloric acid.

EXPERIMENTAL PART.

Benzenesulphonylaminoacetonitrile, $\text{C}_6\text{H}_5\text{SO}_2\text{NHCH}_2\text{CN}$.—This nitrile has previously been prepared by Knoevenagel and Lebach.³ They obtained it by treating benzenesulphonylamide with potassium cyanide and a sodium bisulphite solution of formaldehyde. We have prepared the nitrile by treating aminoacetonitrile⁴ with benzenesulphonyl chloride.

¹ Ber. d. chem. Ges., 24, 3692.

² *Ibid.*, 38, 612.

³ *Loc. cit.*

⁴ Klages: Ber. d. chem. Ges., 36, 1514.

The sulphuric acid salt of aminoacetonitrile was dissolved in water and a layer of benzene poured over the surface of the solution. Benzenesulphonyl chloride and sodium hydroxide solution were then added alternately, in small portions. After the final addition of benzenesulphonyl chloride, the solution was made slightly alkaline and allowed to stand at the ordinary temperature, with occasional shaking. In the course of a few hours the nitrile separated in the layer of benzene as a beautiful, crystalline solid; this was filtered off and purified by crystallizing from benzene. It was insoluble in cold water. It separated from hot water as an oil, which solidified, on cooling, in the form of needles. It melted sharply at 80° with no effervescence. This melting point is somewhat higher than that given by Knoevenagel and Lebach.¹ They state that their product melted at 76° – 77° . Analysis :

	Calculated for $C_8H_8O_2N_2S$.	I.	Found. II.	III.
N	14.28	14.5	14.06	14.24

Benzenesulphonylmethylaminoacetonitrile,

$C_6H_5SO_2N(CH_3)CH_2CN$.—This nitrile was first prepared by allowing methyl iodide to act on the silver salt of benzenesulphonylaminoacetonitrile. It can be obtained more easily by dissolving the nitrile in alcohol containing the calculated amount of sodium ethylate and warming with a molecular proportion of methyl iodide. The reaction is very smooth and the solution is neutral to litmus in a few minutes. After evaporating the alcohol and treating the residue with cold water, to remove sodium iodide, the nitrile remained as a crystalline product. It was deposited from water in beautiful plates and melted, to a clear oil, at 97° . Analysis :

	Calculated for $C_9H_{10}O_2N_2S$.	I.	Found. II.
N	13.33	13.70	13.40

Benzenesulphonylmethylaminoacetic Acid,

$C_6H_5SO_2N(CH_3)CH_2COOH$.—This acid was obtained when benzenesulphonylmethylaminoacetonitrile was digested on the steam-bath with concentrated hydrochloric acid. The saponification is very smooth and the acid separates from the

¹ *Loc. cit.*

warm solution as a colorless, crystalline deposit. It crystallized from hot water in prisms and melted, to a clear oil, at 179° . It was very soluble in alcohol. Analysis :

	Calculated for $C_9H_{11}O_4NS.$	Found.
N	6.11	6.48

Ethyl Benzenesulphonylmethylaminoacetate,

$C_6H_5SO_2N(CH_3)CH_2COOC_2H_5$.—This compound was prepared by esterifying the above acid with alcohol and sulphuric acid. It was obtained as an oil, which showed no signs of solidifying in a freezing mixture. It distilled at 215° – 216° (15 mm.). Analysis :

	Calculated for $C_{11}H_{15}O_4NS.$	Found.
N	5.44	5.29

Behavior of Benzenesulphonylmethylaminoacetic Acid on Hydrolysis.—Eight grams of the acid were boiled with hydrochloric acid for 15 hours. When the acid solution was evaporated to dryness we obtained a semi-solid residue which was somewhat colored. This was dissolved in water and the solution boiled after adding some mercuric oxide. The color was entirely removed by this treatment and a yellow precipitate formed, which was separated by filtration. The filtrate was then saturated with hydrogen sulphide to remove dissolved mercury. After filtering from mercuric sulphide the aqueous solution was evaporated to dryness. We obtained a thick oil, which was extremely soluble in water. On long standing it finally solidified. It separated from its concentrated, aqueous solution in prisms and melted sharply at 136° – 137° . A nitrogen determination agreed with the calculated for the benzenesulphonic acid salt of sarcosine.

	Calculated for $C_9H_{13}O_6NS.$	Found.
N	5.66	5.74

Two and one-half grams of benzenesulphonylmethylaminoacetic acid were heated with concentrated, aqueous ammonia, for 2 hours, at 150° – 155° . When the ammoniacal solution was evaporated to dryness and the residue acidified with sulphuric

acid the unaltered acid was obtained. The acid was again recovered unaltered after heating with concentrated ammonia, at 180° – 190° , for 2 hours.

Benzenesulphonylethylaminoacetonitrile,

$C_6H_5SO_2N(C_2H_5)CH_2CN$.—This nitrile was obtained as an oil which showed no signs of solidifying after standing for 2 weeks. When an attempt was made to purify it by distillation under diminished pressure it slowly decomposed, the chief portion boiling at 225° – 235° (21 mm.). This crude nitrile was used for preparing the acid.

Benzenesulphonylethylaminoacetic Acid,

$C_6H_5SO_2N(C_2H_5)CH_2COOH$.—The acid was easily prepared by successively evaporating the above nitrile with concentrated hydrochloric acid. It crystallized from water in colorless plates, melting at 116° . Analysis :

0.8218 gram substance gave 0.8059 gram $BaSO_4$ (Carius).

	Calculated for $C_{10}H_{13}O_4NS$.	Found.
S	13.16	13.46

Benzenesulphonyl-n-propylaminoacetonitrile,

$C_6H_5SO_2N(C_3H_7)CH_2CN$.—This nitrile was obtained as an oil which refused to solidify after standing for over a month. No attempt was made to distil the nitrile and the crude material was converted into the acid.

Benzenesulphonyl-n-propylaminoacetic Acid,

$C_6H_5SO_2N(C_3H_7)CH_2COOH$.—This acid was obtained by hydrolyzing the above nitrile with concentrated hydrochloric acid. It was purified by repeated recrystallizations from hot water. It separated from its aqueous solution first as an oil, which finally solidified in the form of stout prisms, which melted at 99° – 101° to a clear oil. It was very soluble in the ordinary organic solvents. Analysis :

	Calculated for $C_{11}H_{15}O_4NS$.	Found.
N	5.44	5.85

Benzenesulphonylcarbethoxyaminoacetonitrile,

$C_6H_5SO_2N(COOC_2H_5)CH_2CN$.—The potassium salt of benzenesulphonylaminoacetonitrile, which was prepared according to

Knoevenagel and Lebach's¹ directions, was suspended in benzene and a molecular proportion of ethyl chlorformate added. The solution was then heated on the steam-bath for 10-12 hours, when the reaction was complete. The benzene was evaporated on the steam-bath and the nitrile washed with cold water to remove potassium chloride. The nitrile was insoluble in water. It crystallized from alcohol in the form of sheaves of needles and melted at 83°-85°, without effervescence, to an oil. Analysis :

	Calculated for $C_{11}H_{12}O_4N_2S$.	Found.
N	10.44	10.48

When this nitrile was heated to 50°-60°, with 20 per cent sodium hydroxide solution it dissolved to a clear liquid. Upon acidifying this alkaline solution with hydrochloric or sulphuric acid carbon dioxide was evolved, and an immediate precipitate was obtained. It was identified as unaltered *benzenesulphonylaminoacetonitrile*, melting at 80°. Analysis :

	Calculated for $C_8H_8O_2N_2S$.	Found.
N	14.33	14.55

Benzenesulphonylbenzylaminoacetonitrile,

$C_6H_5SO_2N(CH_2C_6H_5)CH_2CN$.—This nitrile was prepared in the usual way, by acting on the sodium salt of benzenesulphonylaminoacetonitrile with benzyl chloride. It was very soluble in benzene and alcohol, but insoluble in water. It crystallized from dilute alcohol in colorless prisms, melting at 68°-70°. Analysis :

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.79	9.83

Benzenesulphonylbenzylaminoacetic Acid,

$C_6H_5SO_2N(CH_2C_6H_5)CH_2COOH$.—This acid was obtained by prolonged hydrolysis of its nitrile with concentrated hydrochloric acid. It was insoluble in both hot and cold water. It was extremely soluble in alcohol and glacial acetic acid. When the latter solution was diluted with water the acid

¹ *Loc. cit.*

separated first as an oil, which soon solidified in the form of needles. It melted at 123° – 125° . Analysis :

	Calculated for $C_{15}H_{15}O_4NS$.	Found.
N	4.59	4.79

Benzenesulphonyl-p-nitrobenzylaminoacetonitrile,
 $C_6H_5SO_2N(CH_2C_6H_4NO_2)CH_2CN$. — From benzenesulphonylaminoacetonitrile and paranitrobenzyl chloride. It was readily soluble in hot alcohol and separated, on cooling, in the form of prisms. It melted at 123° – 125° . Analysis :

	Calculated for $C_{15}H_{13}O_4N_3S$.	Found.
N	12.68	12.80

Benzenesulphonyl-p-nitrobenzylaminoacetic Acid,
 $C_6H_5SO_2N(CH_2C_6H_4NO_2)CH_2COOH$. — This acid could not be obtained under the same conditions as the preceding acids described in this paper. In order to hydrolyze the corresponding nitrile it was necessary to heat with concentrated hydrochloric acid at 145° – 150° , for 5 hours. It crystallized from alcohol in hair-like needles and melted, with decomposition, at 210° – 212° . Analysis :

	Calculated for $C_{15}H_{14}O_6N_2S$.	Found.
N	8.00	7.61

An attempt was made to hydrolyze this acid to paranitrobenzylaminoacetic acid, by heating with hydrochloric acid. After heating for 6 hours, at 170° – 180° , the acid was recovered unaltered and melting sharply at 210° – 212° , with effervescence. It was again heated for 3 hours, at 200° . Under these conditions the acid was completely decomposed into resinous material.

Ethyl benzenesulphonylcyanmethylaminoacetate,
 $C_6H_5SO_2N(CH_2CN)CH_2COOC_2H_5$. — Benzenesulphonylaminoacetonitrile was dissolved in alcohol containing a molecular proportion of sodium ethylate. To this solution was added the calculated quantity of ethyl chloracetate and it was then heated on the steam-bath until the solution was neutral to litmus. After evaporating the alcohol and treating as usual with water,

an oil, was obtained which finally solidified. It was washed with a cold, dilute solution of sodium hydroxide and then crystallized from benzene and petroleum ether. It crystallized in radiating needles, which melted at 68°-70°. Analysis :

	Calculated for $C_{12}H_{14}O_4N_2S$.	Found.
N	9.92	9.55

2,6-Diketo-4-benzenesulphonylpiperazine,

$$\begin{array}{c}
 C_6H_5SO_2N \\
 \diagdown \quad \diagup \\
 CH_2 \quad CH_2 \\
 | \quad | \\
 CO \quad CO \\
 \diagup \quad \diagdown \\
 NH
 \end{array}$$

This piperazine derivative was obtained when the above ethyl benzenesulphonylcyanmethylaminoacetate was warmed with sodium hydroxide solution, at 53°, until all had dissolved. When the alkaline solution was acidified with hydrochloric or sulphuric acid the piperazine separated in the form of prisms. It melted at 198°-199°, with violent effervescence. Analysis (Kjeldahl) :

	Calculated for $C_{10}H_{10}O_4N_2S$.	Found.
N	11.02	11.17

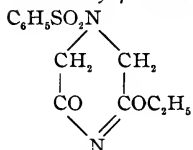
This compound was very stable in contact with concentrated sulphuric acid. It was dissolved in concentrated sulphuric acid and allowed to stand for 3 hours. When water was added to the acid solution the unaltered piperazine separated and melted sharply at 198°-199°. The compound is soluble in sodium hydroxide. Addition of silver nitrate produces a white, crystalline precipitate of the silver salt.

Behavior of 2,6-diketo-4-benzenesulphonepiperazine towards Hydrochloric Acid.—Three and three-tenths grams of the piperazine were heated in a sealed tube, with concentrated hydrochloric acid, for 2 hours, at 140°-150°. On cooling, long, needle-like prisms separated. The hydrochloric acid was evaporated on the steam-bath and the crystalline residue was recrystallized from alcohol. It separated in stout prisms which decomposed, with effervescence, at 225°-240°. The

crystals were free from sulphur but contained chlorine. The compound was extremely soluble in water. It behaved in every respect like the hydrochloric acid salt of imidodiacetic acid, $\text{NH}(\text{CH}_2\text{COOH})_2$.¹ In order to obtain the free acid, the hydrochloride was dissolved in water and digested with an excess of silver oxide. The silver chloride was filtered off and then the excess of silver removed with hydrogen sulphide. When the solution was evaporated a beautiful crop of colorless prisms separated, which decomposed, with violent effervescence, at 235° – 236° . The compound possessed the properties of an acid and a base and agreed in its chemical behavior with the imidodiacetic acid described by Heintz² and Eschweiler.³ Eschweiler states that this acid melts, with decomposition, at about 225° . It has also been our experience that this decomposition point is not definite and varies according to the rate of heating. Analysis (Kjeldahl) :

	Calculated for $\text{C}_4\text{H}_7\text{O}_4\text{N}$.	Found.
N	10.5	10.14

2-Ethoxy-4-benzenesulphonyl-6-ketopiperazine,



—This derivative was obtained when

ethyl iodide was allowed to act, at ordinary temperatures, in ether, on the silver salt of 2,6-diketo-4-benzenesulphonyl-piperazine. After standing for 24 hours the silver iodide was filtered off and the ether solution evaporated to dryness. The ethyl derivative crystallized from alcohol in pyramids and melted sharply at 130° – 132° . Analysis (Kjeldahl) :

	Calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2\text{S}$.	Found.
N	9.9	9.76

Some of this ethoxy derivative was heated in a sealed tube,

¹ Ann. Chem. (Liebig), 136, 213.

² Ibid., 124, 297; 145, 49; 149, 88; 156, 51.

³ Ibid., 278, 232.

with ethyl iodide, for 2.5 hours, at 150° . No molecular rearrangement to the isomeric nitrogen alkyl derivative took place under these conditions. The unaltered piperazine was obtained, melting at 130° – 132° . When mixed with some of the original material the melting point was not lowered.

Benzenesulphonylbenzoylaminoacetonitrile, $C_6H_5SO_2N(COC_6H_5)CH_2CN$.—This nitrile was prepared by suspending the potassium salt of benzenesulphonylaminoacetonitrile in dry benzene and digesting with a molecular proportion of benzoyl chloride, until the reaction was complete. It crystallized from 95 per cent alcohol in radiating needles and melted, to a clear oil, at 110° – 112° . Analysis (Kjeldahl) :

	Calculated for $C_{16}H_{12}O_3N_2S$.	Found.
N	9.33	9.63

When the nitrile was boiled with concentrated hydrochloric acid it was hydrolyzed to a mixture of benzoic acid and benzenesulphonylaminoacetic acid. On prolonged boiling the benzenesulphonylaminoacetic acid was decomposed into resinous material.

Action of Phosphorus Pentachloride on Benzenesulphonylaminoacetic Acid.—Nine grams of benzenesulphonylaminoacetic acid were suspended in acetyl chloride and a slight excess over 1 molecular proportion of phosphorus pentachloride was added. Hydrochloric acid began to be evolved immediately. The solution was allowed to stand for about 12 hours and a few more grams of phosphorus pentachloride were added. After the solution had been allowed to remain for 24 hours it was filtered and the acetyl chloride and phosphorus oxychloride removed by distilling at 100° , in a vacuum. By this means we obtained a tar which was insoluble in benzene and ligroin. It had a strong odor of benzenesulphonyl chloride. The tar was suspended in benzene and warmed with a liberal excess of aniline, for 6 hours. The benzene solution was then filtered and allowed to evaporate spontaneously. After standing a few days large, well-developed prisms separated, which melted sharply at 109° – 110° , to a clear oil. The product was identi-

fied as benzenesulphonylanilide. When the compound was mixed with pure benzenesulphonylanilide the melting point was not lowered. Analysis :

	Calculated for $C_{12}H_{11}O_2NS$.	Found.
N	5.99	5.85

Carbethoxyaminoacetonitrile, $C_2H_5OOCNHCH_2CN$.—This nitrile was obtained as an oil when an aqueous solution of the sulphate of aminoacetonitrile was treated, alternately, in the cold, with sodium hydroxide and ethyl chlorformate. It boiled at 175° (35 mm.). When pure it showed a great tendency to crystallize. It was very soluble in alcohol and benzene. It crystallized from petroleum ether in beautiful, radiating prisms and melted at 48° – 50° , to a clear oil, without effervescence. Analysis :

	Calculated for $C_5H_8O_2N_2$.	Found.
N	21.87	21.85

Action of Benzenesulphonylaminoacetic Acid on Pyrocatechol.—Eight grams of pyrocatechol and 13 grams of benzenesulphonylaminoacetic acid were melted together, at 130° . To the fused material were added 15 grams of phosphorus oxychloride and the mixture heated on the steam-bath. Hydrochloric acid was evolved and the mass assumed a deep red color. After the evolution of hydrochloric acid had practically ceased the product was poured upon finely crushed ice. An oil separated which finally solidified. It was soluble in hot water and was deposited, on cooling, as an oil which afterwards solidified. After recrystallizing from alcohol and benzene it was identified as unaltered benzenesulphonylaminoacetic acid, melting at 166° . Analysis :

	Calculated for $C_8H_9O_4NS$.	Found.
N	6.5	6.2

NEW HAVEN, CONN.,
June 20, 1905.

Contributions from the Chemical Laboratory of the University of Michigan.
GRIGNARD SYNTHESSES IN THE FURFURAN GROUP.

BY W. J. HALE, W. D. McNALLY AND C. J. PATER.

In the course of a series of investigations upon furfuran derivatives our attention has been called to the alcohols of this group. There are, in fact, very few of such compounds known—the only notable case being that of furfuryl alcohol itself.

The Grignard reaction, through the use of the organomagnesium compounds, offers a most serviceable method for preparing these alcohols. Grignard mentions an isolated case of isoamylfurfuryl carbinol,¹ obtained by the action of isoamylmagnesium bromide upon furfuraldehyde. Phenylmagnesium bromide does not react in a similar manner with the aldehyde, but there results only the production of large quantities of diphenyl instead of the anticipated phenylfurfuryl carbinol. It has also been found that benzylmagnesium chloride behaves in the same manner, giving the hydrocarbon dibenzyl.

Turning our attention then from the secondary alcohols, obtainable with difficulty, we find, on the other hand, that the preparation of members of the tertiary class is comparatively easy. For this purpose the esters of pyromucic and dehydromucic acids have been selected. The action of the various organomagnesium compounds upon these esters has served to produce a number of alcohols of varying chemical properties. Owing to the great ease with which hydrochloric and other acids break up such alcohols, their conversion into halides, through the use of phosphorus compounds, is made impossible. In this respect we may compare the action of mineral acids upon the furfuryl alcohol of Wissell and Tollens.² As is best shown in diphenylfurfuryl carbinol, this decomposition is often accompanied with the production of a deep green or blue color, while the residue is a dark red resin. Though the furfuryl group is very sensitive to mineral acids, it is much more

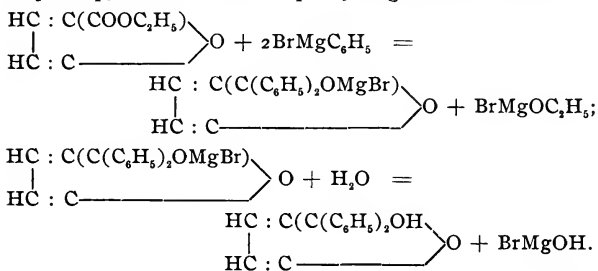
¹ Centrabl., 1901, p. 623.

² Ann. Chem. (Liebig), 272, 295 (1893).

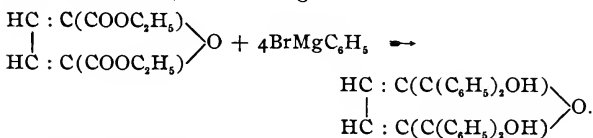
stable when substituted in the α, α' -positions, as in derivatives of dehydromucic acid. None of these alcohols, when perfectly pure, will redden aniline acetate, but, upon standing, the alcohol of the α -furfuryl type slowly undergoes a change, whereby some furfuraldehyde is liberated and hence, upon addition of the aniline salt, the characteristic red color will be developed.

The presence of hydroxyl groups in these alcohols may easily be confirmed by the Tschugaeff reaction,¹ but as a means of further identification, alkyl ethers of the various alcohols were made and analyzed. The method here employed consists in the action of alkyl haloids upon the alkali salts, but is shortened greatly by the use of solid potassium hydroxide with mixtures of the alkyl haloid and the alcohol in question, a method followed by Wissell and Tollens in their work upon furfuryl alcohol. Several attempts were made to prepare esters, as by the use of benzoyl chloride, but only negative results could be obtained, decomposition in most cases having interfered with the process.

The reactions employed may be shown by the following example of pyromucic ester and phenylmagnesium bromide :



In the case of dehydromucic ester we should have, under similar conditions, the following result :



¹ Ber. d. chem. Ges., 35, 3912 (1902).

EXPERIMENTAL.

Diphenyl- α -furfurylcarbinol, $C_4H_3O(C_6H_5)_2 : COH$.—Into a mixture of 15.65 grams brombenzene (2 mols.), and 2.4 grams of magnesium ribbon (2 mols.), all of which had been brought into solution by very gentle boiling for an hour or more under a reflux condenser, on the water-bath, there was gradually added 7 grams (1 mol.) of ethyl pyromucate¹ previously dissolved in dry ether. The reaction takes place almost immediately and, after 3–4 hours' further boiling, a deep, purple color is seen to have developed, while a solid substance separated out. The whole is now treated with cold water to decompose the magnesium compound and enough dilute acetic acid added to effect complete solution of the magnesium salts. To the clear contents of the vessel more ether is added and the ethereal layer removed. The residue obtained from this ether extract was now distilled with steam, in order to remove any unchanged ester or brombenzene that may possibly be present. Only a small amount of diphenyl was seen to collect in the distillate, while from the distilling flask the light brown, solid product was removed and placed upon porous plate to dry. This alcohol may be purified by crystallization from low boiling ligroin (40°–60°). The yield is 70 per cent of the theory. Diphenyl- α -furfuryl carbinol is soluble in ether, alcohol, chloroform, benzene, ethyl acetate, or in warm ligroin, crystallizing from the last in beautiful, colorless, rhombic prisms, melting at 92°.4 (corr.).

0.1752 gram substance gave 0.5222 gram CO_2 and 0.0905 gram H_2O .

	Calculated for $C_{17}H_{14}O_2$.	Found.
C	81.56	81.31
H	5.64	5.78

Diphenyl- α -furfuryl carbinol resembles, in many respects, the furfuryl alcohol of Wissell and Tollens.² Though its sensibility to mineral acids is not so marked, it readily undergoes decomposition with dilute hydrochloric acid into a resin-like

¹ Ann. Chem. (Liebig), 25, 276 (1838).

² *Ibid.*, 272, 295 (1893).

substance. Upon warming this alcohol with hydrochloric acid the green color at first developed passes into a deep purple or violet, a condition more readily obtainable when anhydrous acid is employed. Heating with water at high temperatures effects a decomposition of the alcohol, and even upon standing in the air or in vacuum for a short period the alcohol melts into a gummy mass, acquiring, simultaneously, a dark red color. For a few days this alcohol may be preserved by suspension in ligroin.

Methyl Ether of Diphenyl- α -furfuryl Carbinol,

$C_4H_9O(C_6H_5)_2 : COCH_3$.—This ether was prepared in the same manner as furfuryl methyl ether,¹ the simplest of the class of furfuryl ethers. Four grams of the alcohol were dissolved in 5 grams of methyl iodide and to the solution, kept cool by an ice mixture and shaken, there was gradually added 2 grams of finely pulverized potassium hydroxide. The mixture slowly warms up to the boiling-point and is finally removed to a water-bath, where it is gently warmed, under a reflux condenser, till no further action is noticed. A small quantity of water is now added and the alcoholic layer removed by extraction with ether. This ether extract was thoroughly dried over calcium chloride and then a small piece of sodium dropped into it, to unite with any unchanged alcohol. Only the slightest amount of hydrogen escaped, hence the action must have been practically complete. The filtered ether extract was now evaporated and the pleasant smelling product submitted to distillation, *in vacuo*. A colorless oil passes over at 206° – 207° (26 mm.). This colorless distillate has sp. gr. 1.1195 at 20° . Upon standing it gradually acquires a yellow color and, like the alcohol itself, is very sensitive to the action of mineral acids, undergoing, thereby, a decomposition into resinous substances. The yield of the ether is quantitative.

0.3092 gram substance gave 0.9280 gram CO_2 and 0.1701 gram H_2O .

¹ Ann. Chem. (Liebig), 272, 296 (1893).

	Calculated for $C_{18}H_{16}O_2$.	Found.
C	81.78	81.86
H	6.09	6.15

Diethyl- α -furfuryl Carbinol, $C_4H_3O(C_2H_5)_2 : COH$.—Into an ethereal solution of ethylmagnesium iodide, prepared from 2.4 grams magnesium and 15.6 grams ethyl iodide, there was gradually added an ethereal solution containing 7 grams ethyl pyromucate. After 3 hours' boiling under a reflux condenser the reaction is completed. The mixture was treated with water containing only enough acetic acid to effect solution and then extracted with ether. The ether extract, freed from the presence of any acid by sodium carbonate and dried over calcium chloride, was allowed to evaporate in a vacuum desiccator. The product obtained could not be purified by distillation, owing to the ease with which it underwent decomposition, but it is undoubtedly the diethyl- α -furfuryl carbinol. It is light yellow in color and possesses a pleasant, ethereal color. Upon standing it was seen to become dark; finally, by placing it in a vacuum desiccator, this color increased in depth until, after a few days, the whole was found to have solidified to a dark brown, crystalline mass, having undergone, therefore, a complete transformation into another derivative.

1-Methyl-2-ethyl- α -furfuryl Ethylene,

$C_4H_3OC(C_2H_5) : CHCH_3$.—This ethylene derivative is most naturally to be expected from the foregoing alcohol as the result of dehydration, a condition often brought about in these tertiary alcohols by long standing. The molecule of water thus lost from the hydroxyl group and a hydrogen atom of an ethyl group in the diethylfurfuryl carbinol, may much more readily be eliminated through the agency of gentle heat. In many cases this conversion into unsaturated hydrocarbons has been most effectively carried out through the use of dehydrating agents.¹ Upon crystallization from ethyl acetate the product appeared in fine, long, colorless needles. Several crystallizations quickly made gave a product not so crystalline,

¹ Béhal: *Compt. rend.*, **132**, 480 (1901). Tissier and Grignard: *Ibid.*, **132**, 1182 (1901). Klages: *Ber. d. chem. Ges.*, **35**, 2646 (1902). Hell: *Ibid.*, **37**, 225, 230 (1904).

but if the crystallization is carried out slowly the needles at first formed pass over into a second, more stable variety, that of small, colorless, rhombic prisms. This 1-methyl-2-ethyl- α -furfuryl ethylene is soluble in chloroform, benzene, carbon bisulphide, ether or ligroin. It is soluble in warm acetone or ethyl acetate, from either of which it may be crystallized. It is insoluble in water and but sparingly soluble in hot alcohol. A solution of bromine in carbon bisulphide is immediately decolorized by this compound. The best defined rhombic prisms are obtained by crystallization from ethyl acetate and give the constant melting point 249° (corr.).

0.1066 gram substance gave 0.3100 gram CO_2 and 0.0866 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{12}\text{O}$.	Found.
C	79.36	79.31
H	8.88	9.08

The action of methylmagnesium iodide upon pyromucic ester gave a red-colored liquid of pleasant odor, but, owing to its instability, nothing could be done with it.

Dibenzyl- α -furfuryl Carbinol, $\text{C}_4\text{H}_3\text{O}(\text{C}_6\text{H}_5\text{CH}_2)_2 : \text{COH}$.—Into an ethereal solution of benzylmagnesium chloride,¹ prepared from 0.96 gram magnesium and 5.04 grams benzyl chloride, there was gradually added 5.6 grams of ethyl pyromucate, dissolved in dry ether. After 3 hours' boiling, under a reflux condenser, upon a water-bath, the reaction was at an end; in the meantime a yellow solid had separated out upon the walls of the flask. The entire contents of the flask were now decomposed with cold water, previously acidulated with acetic acid, and the resulting clear solution extracted with ether. This ethereal extract, freed from its ether, was subjected to distillation by steam for a half hour or more, after which the solid product that collects upon the walls of the vessel was again taken up in ether, the ethereal solution dried over calcium chloride and then allowed to evaporate. Dibenzyl- α -furfuryl carbinol is very soluble in ether, chloroform, benzene, carbon bisulphide, or acetone; fairly soluble in alcohol and insoluble

¹ Ber. d. chem. Ges., 37, 455 (1904).

in water. It is soluble in hot ligroin, from which it crystallizes in beautiful, silky needles showing a constant melting-point of $82^{\circ}.7$ (corr.). This alcohol is much more stable than the corresponding diphenyl derivative. It does not decompose by standing but, through the action of strong hydrochloric acid, rapidly assumes a deep green color, undergoing at the same time complete decomposition.

0.1682 gram substance gave 0.5053 gram CO_2 and 0.1008 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{18}\text{O}_2$.	Found
C	81.98	81.94
H	6.52	6.70

Methyl Ether of Dibenzyl- α -furfuryl Carbinol, $\text{C}_4\text{H}_3\text{O}(\text{C}_6\text{H}_5\text{CH}_2)_2 : \text{COCH}_3$.—Into a mixture of 2 grams of the alcohol with 2.5 grams of methyl iodide contained in a flask, kept cool by ice-water, there was gradually added 1 gram of finely pulverized potassium hydroxide. The reaction is conducted in the same manner as described under the preparation of methyl diphenyl- α -furfuryl ether. From the ether extract, as finally obtained, there separated a yellow, crystalline compound. This methyl ether is extremely soluble in all of the ordinary media, though but fairly soluble in warm alcohol and insoluble in water. It may, however, with care, be crystallized from low boiling ligroin (40° – 60°) in which it dissolves by gentle warming. The crystals appear in long, colorless needles, melting at $61^{\circ}.2$ (corr.).

0.1505 gram substance gave 0.4524 gram CO_2 and 0.0956 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_2$.	Found.
C	82.15	81.99
H	6.90	7.10

Tetraphenyl- α, α' -furfuryl Dicarbinol, $\text{C}_4\text{H}_2\text{O} : [\text{C}(\text{C}_6\text{H}_5)_2\text{OH}]_2$.—Into an ethereal solution of phenylmagnesium bromide, containing 2.4 grams of magnesium and 15.7 grams of brombenzene, there was gradually added 5.3 grams ethyl dehydromucate,¹ dissolved in dry ether. After boiling the contents of

¹ Ann. Chem. (Liebig), 193, 190 (1878).

the flask over a water-bath for some 4 hours and allowing it to stand over night, a sufficient quantity of water, containing acetic acid, was added and the whole thus brought into solution. The ethereal layer, upon decantation, was freed from ether and distilled with steam, in order to remove any unchanged ester that may be present; in this case only small quantities of diphenyl were collected in the distillate. The yellow mass remaining in the distilling flask was now taken up in ether and the ethereal solution warmed with a small amount of bone-black, filtered, dried over calcium chloride and allowed to evaporate; a light yellow residue was obtained, amounting to about 60 per cent of the theoretical yield. Tetraphenyl- α, α' -furfuryl dicarbinol is soluble in alcohol, ether, acetone, or chloroform, readily soluble in benzene and almost insoluble in ligroin. It dissolves easily in hot carbon bisulphide, crystallizing out on cooling. It is insoluble in water. From solution in ether and ligroin, its best solvent, there is thrown out, upon spontaneous evaporation, small, colorless, rhombic crystals. These, after several crystallizations, melted at $165^{\circ}.5$ (corr.) to a pure, red liquid. This alcohol is more stable than the corresponding diphenyl- α -furfuryl carbinol. It may be preserved for some time, though, on standing, it soon acquires a distinct yellow color. Strong mineral acids decompose it, but not with the same ease with which they act upon diphenyl- α -furfuryl carbinol.

0.2207 gram substance gave 0.6722 gram CO_2 and 0.1126 gram H_2O .

	Calculated for $\text{C}_{30}\text{H}_{24}\text{O}_3$.	Found.
C	83.30	83.07
H	5.59	5.71

Methyl Ether of Tetraphenyl- α, α' -furfuryl Dicarbinol,
 $\text{C}_4\text{H}_2\text{O} : [\text{C}(\text{C}_6\text{H}_5)_2\text{OCH}_3]_2$.—In the same manner as described under the preparation of diphenyl- α -furfuryl carbinol ether, 2 grams of tetraphenyl- α, α' -furfuryl dicarbinol were treated with an excess of methyl iodide (5 grams) and potassium hydroxide (2 grams). The dry ether extract was allowed to evaporate *in vacuo* as, otherwise, only a viscous mass could be obtained.

The crystalline residue could most readily be freed from impurities by digesting it, in the cold, with low boiling ligroin (40° – 60°). The remaining portion was next taken up in warm ligroin of the same boiling-point and the solution set in a vacuum desiccator to crystallize. In this manner a white product appeared which, after several similar crystallizations, gave the pure methyl ether. This methyl ether is very soluble in chloroform, ether, benzene, acetone, carbon disulphide, or high boiling ligroin. It is sparingly soluble in low boiling ligroin or alcohol and insoluble in water. The pure ether crystallizes best from alcohol, in white needle clusters, melting at $88^{\circ}.2$ (corr.). When exposed to the air it gradually melts to an indistinct mass.

0.1298 gram substance gave 0.3966 gram CO_2 and 0.0742 gram H_2O .

	Calculated for $\text{C}_{32}\text{H}_{28}\text{O}_8$.	Found.
C	83.44	83.33
H	6.13	6.39

Ethyl Ether of Tetraphenyl- α,α' -furfuryl Dicarbinol, $(\text{C}_4\text{H}_2\text{O}) : [\text{C}(\text{C}_6\text{H}_5)_2\text{OC}_2\text{H}_5]_2$.—By the action of potassium hydroxide upon a solution of tetraphenyl- α,α' -furfuryl dicarbinol, in ethyl iodide, in accordance with the method described in the preparation of the previous ethers, the ethyl ether of this alcohol was readily obtained. The product has a fine, crystalline appearance and is very soluble in alcohol, ether, acetone, or chloroform; fairly soluble in benzene or carbon bisulphide; insoluble in water and almost insoluble in ligroin. It may best be crystallized out of ether and ligroin, from which it appears in rhombic prisms, melting at 171° (corr.). The ethyl ether is a much more stable compound than the corresponding methyl ether. Upon standing it slowly acquires a distinctive yellow color and, when melted, undergoes decomposition into a red product.

0.1489 gram substance gave 0.4564 gram CO_2 and 0.0899 gram H_2O .

	Calculated for $C_{24}H_{22}O_3$.	Found.
C	83.56	83.60
H	6.60	6.75

The preparations of tetraethyl- and tetramethyl- α,α' -furfuryl dicarbinols were attempted but the light red colored liquids obtained could not be satisfactorily worked up. They possessed a most pleasant ethereal odor and slowly underwent decomposition, even at ordinary temperatures.

Tetrabenzyl- α,α' -furfuryl Dicarbinol,

$C_4H_2O : [C(C_6H_5CH_2)_2OH]_2$.—Into a solution of benzylmagnesium chloride, prepared from 2.3 grams magnesium and 12 grams of benzyl chloride, in dry ether, an ethereal solution of 5 grams of ethyl dehydromucate was slowly added. After some 3 hours' boiling upon the water-bath the reaction is at an end, the product was allowed to stand a short time and was then decomposed, in the usual way, with water containing acetic acid. The whole was then extracted with ether, which, in turn, must be freed from any acid by sodium carbonate and then dried over calcium chloride. The residue from the ether extract was now submitted to distillation with steam for a short time, to remove any unchanged ester and the dibenzyl usually present. The yellow substance thus left in the distilling flask was again taken up in ether, treated with bone-black, dried over calcium chloride and then allowed to evaporate in a vacuum desiccator. The residue was an extremely viscous mass, which refused to crystallize even after long standing. Application of low temperature easily brought about a solidification, but not in the crystalline form. This solid product becomes viscous again at 5° – 6° . Tetrabenzyl- α,α' -furfuryl dicarbinol is a fairly stable alcohol, of a light straw color, possessing a very agreeable odor. It is soluble in all the ordinary media excepting ligroin and water. From mixtures of ligroin with the other solvents no crystalline product could be obtained, in every case the deposited substance was viscous. The alcohol boils at 193° – 195° (30 mm.) but, as a great portion hereby undergoes decomposition, only a small

quantity of pure product can be collected. The sp. gr. of the alcohol is 1.126 at 27°.

0.1758 gram substance gave 0.5374 gram CO₂ and 0.1046 gram H₂O.

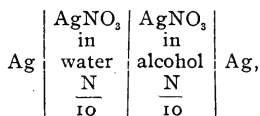
	Calculated for C ₃₄ H ₃₂ O ₃ .	Found.
C	83.56	83.38
H	6.60	6.66

ANN ARBOR, MICH.,
July 22, 1905.

SOME CONCENTRATION CELLS IN METHYL AND ETHYL ALCOHOLS.

BY J. HUNT WILSON.

Although within the last two decades measurements of concentration cells, for the purpose of verifying the equations of Nernst and Planck, have been numerous, such measurements have been almost wholly restricted to aqueous solutions. Up to the present time I have been unable to find any measurements recorded of a non-aqueous concentration cell. Jones¹ measured some cells of the type



in an attempt to calculate the percentage of ionization in the alcoholic solutions, but found that the solution tension of Ag has a value much smaller in alcoholic solutions than in water. He calculated the ratio to be about 1 : 42 to 1 : 48.

Campetti² gives the results of some measurements similar to those of Jones. He worked with solutions of NH₄Cl, LiCl, ZnCl₂, CuCl₂, CdCl₂, ZnI₂, CdI₂, in both water and alcohol. To determine the potential differences he made use of the "dropping electrode." He states, as did Jones, that the alcoholic solution is positive in reference to the aqueous solution.

¹ Z. physik. Chem., 14, 346.

² *Ibid.*, 14, 374.

My object in taking up the following work was to determine the electromotive force of a few non-aqueous concentration cells.

As the formula of Nernst is based on the theory of electrolytic dissociation, its ability to predict the electromotive force of a non-aqueous concentration or liquid cell would largely depend on the extent to which the theory of ionization could be applied to such solutions. Restricted to aqueous solutions, the theory of electrolytic dissociation serves to correlate and explain observed phenomena very clearly, but its extension to non-aqueous solutions has, in many instances, given rise to anomalies which can only be harmonized with the theory by the introduction of ideas of the association of both solvent and solute and of combination between both. In all cases, however, it serves as an admirable "working hypothesis."

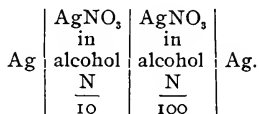
Two formulas are available for calculating the electromotive force of a concentration cell. The first of these, that of Helmholtz, is independent of the ionic theory and calculates the electromotive force from the vapor pressures of the two solutions of the cell. The formula of Nernst is based on the ionic theory, and involves a knowledge of the transport numbers of the dissolved substance and of the osmotic pressures of the solution. In the formula

$$\pi = 0.0002 \frac{2v}{u+v} \cdot T \cdot \log \frac{p_1}{p_2}$$

the ratio $\frac{p_1}{p_2}$ is commonly set equal to the ratio of the molecular concentration. In dilute, aqueous solutions this is approximately correct, but in concentrated, aqueous solutions and in non-aqueous solutions of low ionizing power, it would cause a large error due to incomplete dissociation. In such cases the ratio of the ionic concentrations as calculated from the conductivities is substituted for the ratio of the osmotic pressures.

The choice of a non-aqueous concentration cell for measurement and calculation of its electromotive force is rather diffi-

cult. While of late years measurements of the conductivities of non-aqueous solutions have been numerous, there are very few compounds, the transport numbers of which are known for a non-aqueous solvent. Silver nitrate is soluble, however, in both methyl and ethyl alcohol, and as values of the conductivities and transport numbers of this salt are available for these solvents, I have undertaken the measurement of some cells of the type

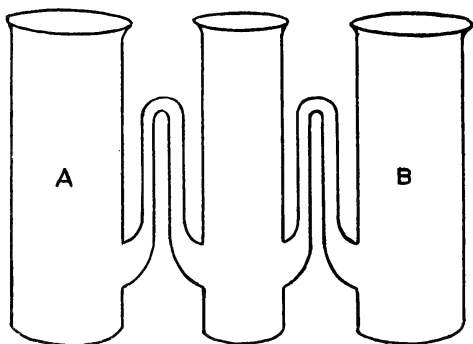


EXPERIMENTAL PART.

All the methyl and ethyl alcohol used in the following work was purified by distillation from lime, anhydrous copper sulphate and, finally, from sodium. Even alcohol thus purified gave a slight discoloration with silver nitrate, but I found that, by distilling with a small quantity of silver nitrate, a product was obtained which gave a clear solution. The silver nitrate used was crystallized from water, dried, fused at a gentle heat and then powdered. In distilling the alcohols and in preparing the solutions, moisture was excluded as far as possible by the use of tubes filled with phosphorus pentoxide. All the measurements of electromotive force were made by the compensation method, with a D'Arsonval galvanometer as zero instrument. The vessel used to contain the cells was of the form on the opposite page.

The siphon tubes from each half cell were fused into a connecting vessel instead of being immersed in it, as this facilitated the exclusion of moisture and made the cell more compact and easier to handle in the thermostat. The top of each tube was closed by means of a tightly-fitting rubber stopper, through which passed a drying tube filled with phosphorus pentoxide. The electrodes were of silver foil and were coated with electrolytic silver before use. The glass tubes carrying the electrodes were pushed through the rubber stoppers of the tubes designated A and B in the figure.

For the measurements at 25° the cell was placed in an Ostwald thermostat, for those at 0° it was packed in finely crushed ice. Solutions of silver nitrate, in methyl alcohol, of four



different concentrations were made up. The first solution was prepared by direct weighing, the others by diluting portions of the original solution. The following table gives the concentration, in liters per gram-molecule (v) and the molecular conductivity μ , at both 25° and 0°. The values of the conductivities are taken from the recent work of Jones and Bassett:¹

v .	μ_v 0°.	μ_v 25°.
10	25.96	35.77
40	39.71	53.42
160	51.09	70.36
640	61.42	88.24

Concentration cells were then prepared with these various solutions and their electromotive force measured. In the following tables $v'-v''$ represent the concentrations of the two solutions used in the cell, b the observed electromotive force, and c the value of the electromotive force calculated from the formula of Nernst :

¹ THIS JOURNAL, 32, 420.

At 25°.

$v'-v''$,	<i>b.</i>	<i>c.</i>
10-40	0.021	0.029
—160	0.044	0.062
—640	0.086	0.098
40-160	0.031	0.033
—640	0.065	0.068
160-640	0.035	0.034

At 0°.

$v'-v''$,	<i>b.</i>	<i>c.</i>
10-40	0.018	0.026
—160	0.034	0.057
—640	0.067	0.090
40-160	0.028	0.032
—640	0.061	0.064
160-640	0.031	0.033

In calculating the above results allowance was made for incomplete dissociation by introducing the ratio of the ionic concentration into the formula in place of the molecular concentrations. The value of the ionic concentration was obtained from the expression $\frac{\mu_v}{\mu_\infty} \times m$, where $\frac{\mu_v}{\mu_\infty}$ represents the degree of dissociation and m the molecular concentration.

Solutions of silver nitrate in ethyl alcohol were then prepared of the following concentrations :

<i>v.</i>	μ_v 0°.	μ_v 25°.
38.86	11.35	16.96
155.47	15.13	23.87
621.89	19.43	30.62

These values are also taken from the results of Jones and Bassett.¹ Cells were made up and measured as previously described :

At 25°.

Cell.	<i>b.</i>	<i>c.</i>
38.86-621.89	0.067	0.067
—155.47	0.029	0.032
155.47-621.89	0.038	0.035

¹ *Loc. cit.*

At 0°.

Cell.	b.	c.
38.86-621.89	0.055	0.062
—155.47	0.027	0.032
155.47-621.89	0.035	0.031

A close comparison between the observed and calculated values will show that the agreement is quite good in most cases. With the exception of the cells containing N/10 AgNO_3 in methyl alcohol the difference between the observed and calculated values is less than 0.05 volt, except in the first ethyl alcohol cell measured at 0°, where there is a difference of 0.07 volt. With these exceptions the agreement of values is fully as good as is commonly obtained with aqueous solutions.

Before attempting to account for the poor agreement in N/10 methyl alcohol cells it would be advisable to confirm these values by additional measurements, although it is hardly possible that the difference is due to experimental errors, as all the measurements were made in duplicate.

It should be stated here that the Nernst formula can hardly be regarded as giving more than approximate values. The formula presupposes the absence of any molecular aggregation of dissolved molecules, or any combination between solvent and solute. These phenomena are of common occurrence in both aqueous and non-aqueous solutions. Also, when we consider the uncertainty of the value of μ_∞ for both alcohols, the above agreement must be considered satisfactory.

In the calculation values given above, 98 was taken as the value of μ_∞ for silver nitrate in methyl alcohol, while 35.5 was used as the most probable value of μ_∞ in the ethyl alcohol solutions.¹

From the results obtained in this work I am led to believe that the Nernst formula will be found to hold as well in non-aqueous as in aqueous solutions, but more extensive measurements of non-aqueous concentration cells are necessary before this can be assured. In the near future I hope to publish some measurements of concentration cells with pyridine as the solvent.

¹ Jones : Z. physik. Chem., 14, 354.

In conclusion, I desire to express my thanks to Dr. C. J. Thatcher for valuable suggestions and criticism during the course of this work.

EASTON, PA.,
July 20, 1905.

A PERIODIC RELATION BETWEEN THE ATOMIC WEIGHTS AND THE INDEX OF REFRACTION.

BY F. L. BISHOP.

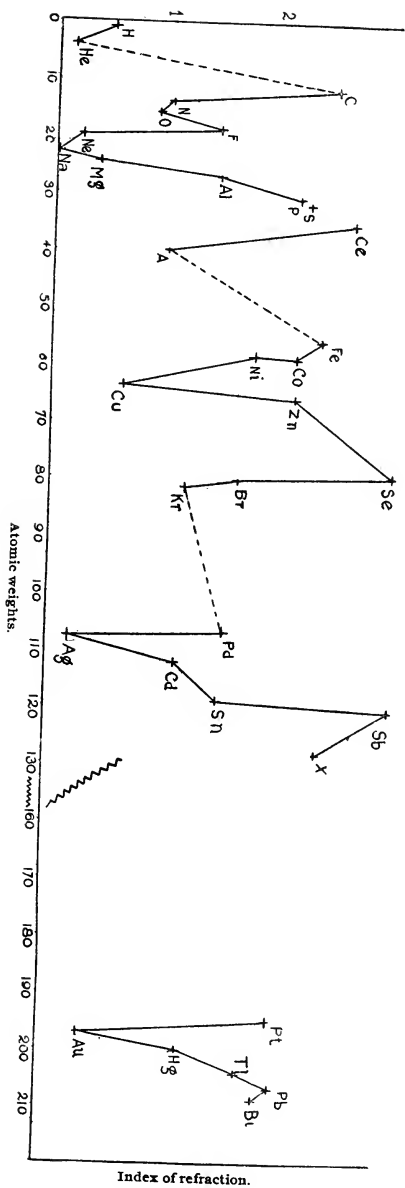
The absolute establishment of a periodic relation between the atomic weights and the index of refraction would require the accurate determination of the index of refraction for a number of elements which have never been investigated. However, Professor Paul Drude¹ has made a study of the index of refraction of many of the opaque elements, while for the transparent bodies there are, in most instances, numerous determinations. In the case of gases the refractivity has been accurately determined by the method suggested by Lord Rayleigh.²

The data at present available for illustrating this periodic relation are given in the following table, where the elements are arranged in the order of increasing atomic weights:

Element.	Atomic weight.	Index.
H	1.008	0.473
He	4.00	0.124
C (diamond)	12.00	2.46
N	14.04	1.02
O	16.00	0.924
F	19.00	1.434
Ne	20.00	0.235
Na	23.05	0.005
Mg	24.36	0.373
Al	27.1	1.44
P	31.0	2.14
S	32.0	2.24
Cl	35.45	2.62
A	39.9	0.968
Fe	55.9	2.36

¹ Wied. Ann., **39**, 513 (1890).

² P. Roy. Soc., **59**, 206 (1895).



Element.	Atomic weight.	Index.
Ni	58.7	1.79 } ?
Co	59.0	2.12 } ?
Cu	63.6	0.641
Zn	65.4	2.12
Se	79.2	2.98
Br	79.96	1.65
Kr	81.8	1.45
Pd	107.0	1.54 <i>red</i>
Ag	107.93	0.181
Cd	112.4	1.13
Sn	119.0	1.48
Sb	120.2	3.04
X	128.0	2.36
Pt	194.8	2.06
Au	197.2	0.366
Hg	200.0	1.73
Tl	204.1	1.75
Pb	206.9	2.01
Bi	208.5	1.90

The index is that of sodium light at 20° , and the gases are under standard pressure.

The values obtained by Drude are used, even when later determinations are available, in order that the same instrumental errors may be present.

The maxima and minima are best studied from the curves (*vide* p. 85).

It is seen that the minima of the well defined groups are Na, Cu, Ag, Au, which are metals in the first group of Mendeléeff's periodic table. The periodicity is, perhaps, best shown in the series from C to Cl, as we have in this series the index for all the elements.

It is evident from the methods of measurement of the index for opaque substances that there is opportunity for more or less error, it is not the purpose of this preliminary note, however, to discuss methods, but to note the apparent periodic relation between the atomic weights and the index of refraction of the elements.

NOTE.

The Preparation of Benzonitrile.

In the course of some work which was being carried out in this laboratory in 1904, it was necessary to provide rather large quantities of benzonitrile; at my suggestion, therefore, Messrs. E. J. Hoffman, and W. A. Syme studied some of the various methods which have been proposed for the preparation of this compound. Their results, which may be of use to others, are recorded in the following table; they have been checked, in most cases, by other students. The figures given for the cost are believed to be accurate *relatively*, the *absolute* cost is, necessarily, variable. In reckoning the time no account was taken of the washing and distillation of the crude product, as this was practically the same in all cases; the time required to dry an ethereal solution, when this was needful, has also been disregarded, because it did not occupy the worker. The yield refers to material which has been distilled.

Method I.—Sandemeyer's reaction:¹ Aniline 35 grams, copper sulphate crystals 100 grams, potassium cyanide 110 grams, sodium nitrite 25 grams and hydrochloric acid 50 grams were employed.

Method II.—From benzamide 15 grams and phosphoric anhydride 25 grams.²

Method III.—From benzoic acid 100 grams and lead thiocyanate 240 grams.³

Method IV.—From sodium benzenesulphonate 100 grams and potassium cyanide 100 grams.⁴

Method V.—From benzamide 23 grams and quicklime in excess.⁵

Method VI.—From benzoic acid 50 grams and potassium thiocyanate 20 grams.⁶

As was to be expected Mr. Syme did not obtain a large yield of benzonitrile by the use of iodobenzene and silver cyanide,⁷ nor was he able to get satisfactory results by the distillation of aniline oxalate.⁸ He prepared benzamide very easily and quickly from benzoic acid and ammonium thiocyanate.⁹

¹ Ber. d. chem. Ges., **17**, 2653.

² Hofmann and Buckton : Ann. Chem. Pharm., **100**, 155.

³ Krüss : Ber. d. chem. Ges., **17**, 1766.

⁴ Merz : *Ibid.*, **3**, 710.

⁵ Anschütz and Schulz : Ann. Chem. Pharm., **196**, 48.

⁶ Letts : Ber. d. chem. Ges., **5**, 673.

⁷ Merz and Weith : *Ibid.*, **10**, 746.

⁸ A. W. Hofmann : Compt. rend., **64**, 388.

⁹ Kekulé : Ber. d. chem. Ges., **6**, 113.

Method.	Yield. Grams.	Per cent of the theoretical.	Time.	Cost of 100 grams.
I	25	64	About 4 hours	\$0.72
II	12	95	" I "	\$1.00
III	60	71	" 10 "	\$0.55
IV	15	26	" I "	\$5.86
V	8.2	42	I "	\$1.70
VI	12.2	58	3 "	\$1.15

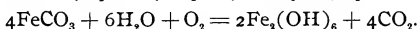
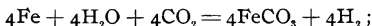
J. BISHOP TINGLE.

JOHNS HOPKINS UNIVERSITY,
January, 1905.

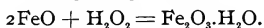
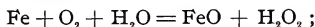
REPORTS.

The Rusting of Iron.

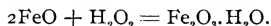
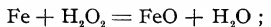
In presenting the subject of chemistry to a class just beginning the study of that science, the rusting of iron is often given as an example of a familiar chemical action. The commonly accepted explanation of this change is that given by Grace Calvert and Crum Brown. According to these authors it is due to the combined action of the oxygen and carbon dioxide of the air in the presence of liquid water and should be represented by the following equations:



In a recent paper¹ Dunstan, Jowett and Goulding show that the action does not require the presence of carbon dioxide and that the inhibiting action of alkalies is not due to their power of absorbing this substance. The results show that, although hydrogen peroxide cannot actually be detected during the rusting of iron, it is probably formed as an intermediate product of the change. The results of these experiments support Traube's view of the nature of such oxidation processes, *viz.*, that the water is decomposed by the iron, the liberated hydrogen forming hydrogen peroxide with the dissolved molecular oxygen, involving the assumption that hydrogen peroxide is not "oxidized water;" but "reduced or hydrogenized oxygen." According to the authors the reactions involved should be represented by the equations:

¹ J. Chem. Soc., 88, 1548 (1905).

The excess of hydrogen peroxide immediately reacting with the iron to form a further quantity of rust thus:



It is shown, in support of this theory, that many substances which decompose hydrogen peroxide and therefore interfere with its existence, likewise prevent the rusting of iron, while bodies which are incapable of decomposing hydrogen peroxide do not prevent the rusting. In the atmospheric oxidation of lead and zinc the formation of hydrogen peroxide has been actually detected, and the substances which prevent the action in the case of iron act in a similar manner with lead and zinc. Parallel series of experiments, when the duration of the experiments was as much as 3 months, show that iron does not rust when left in contact with dry gases, nor does it rust when in contact with moist oxygen or a mixture of moist oxygen and carbon dioxide so long as the temperature is kept constant, whereby the deposition of liquid water on the metal is prevented. With a fluctuating temperature it rusts in moist oxygen, and in a mixture of moist oxygen and carbon dioxide; but not in carbon dioxide alone nor in a mixture of moist oxygen and ammonia. Whitney supposed the rusting to be due to a slight dissociation of the water into H and OH ions and to a solution of minute quantities of iron, owing to the formation of an electric circuit, to form ferrous hydroxide which would absorb oxygen from the air. If this explanation is correct the hydrogen should escape as a gas and substances such as alkalis, by hindering the accumulation of H ions, should interfere with rusting or entirely prevent it, while acids and some salts should accelerate it, as they increase the accumulation of H ions. The authors, however, could obtain no evidence of the formation of hydrogen and proved that substances such as chromic acid prevent the rusting; they also showed that if part of the water which had been in contact with iron for 3 weeks, without any visible change having taken place, was quickly poured off when the vessel was opened, and was then allowed to stand in the air, no precipitation of iron salts took place nor could any trace of iron be detected in the solution, while the iron which was left in the water quickly rusted when air was allowed to come in contact with the water covering the iron.

A study of the action of carbon dioxide under different conditions, including a repetition of Grace Calvert's work, showed that the small amount of carbon dioxide in the air could

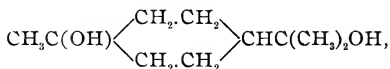
play only a very subordinate part in the ordinary rusting of iron, especially as it has been proved that rusting proceeds rapidly in the total absence of carbon dioxide.

The authors demonstrated that the process of "rusting" is different from other processes in which iron undergoes oxidation with the formation of ferric hydroxide, and conclude, therefore, that iron, oxygen and *liquid* water are alone necessary for the rusting of iron.

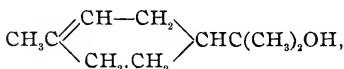
J. E. G.

Grignard's Reaction.

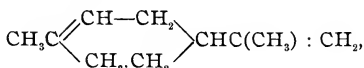
Since the publication of the previous report,¹ papers dealing directly or indirectly with this subject have appeared in scarcely lessened numbers; only the more important of them will be referred to in the present communication. W. H. Perkin, Jr.,² has synthesized terpin,



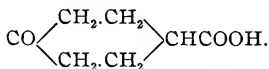
terpineol,



and dipentene (limonene),



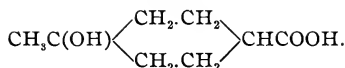
by the following steps: Ethyl β -iodopropionate and ethyl sodiocyanoacetate yield ethyl γ -cyanopentane- α, γ, ϵ -tricarboxylate, $\text{C}_2\text{H}_5\text{OCOC}(\text{CN})(\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5)_2$; concentrated hydrochloric acid converts this into pentane- α, γ, ϵ -tricarboxylic acid, $\text{HOCOCH}(\text{CH}_2\text{CH}_2\text{COOH})_2$, which, when digested with acetic anhydride and distilled, passes into δ -keto-hexahydrobenzoic acid,



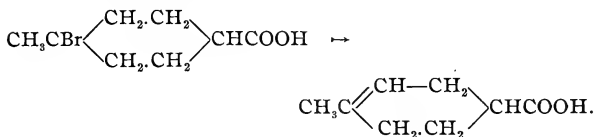
The ester of this acid is treated with methylmagnesium iodide and the product hydrolyzed, when there is obtained δ -hydroxyhexahydroparatoluic acid,

¹ THIS JOURNAL, 33, 304 (1905).

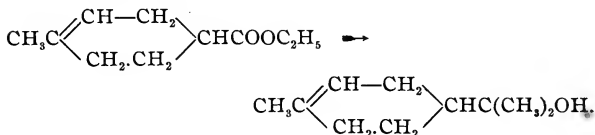
² J. Chem. Soc., 85, 654 (1904).



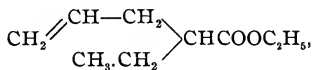
Fuming hydrobromic acid converts this into the corresponding bromo acid which, under the influence of pyridine, passes into Δ^3 -tetrahydroparatoluic acid,



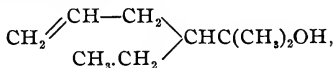
From the ester of the unsaturated acid methylmagnesium iodide yields terpineol,



Terpineol is readily converted into dipentene and terpin hydrate by the action of potassium hydrogen sulphate and dilute sulphuric acid, respectively. Apart from its other interest, this synthesis may be regarded as settling, beyond dispute, the question of the constitution of the three hydrocarbons concerned. In subsequent papers,¹ Perkin and his co-workers describe syntheses of other, hitherto unknown, terpenes, by the same series of reactions using Δ^1 -tetrahydroparatoluic acid, and also the preparation, from ethyl allylacetate, of the open chain compounds, ethyl ethylallylacetate,

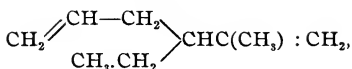


dimethylethylisobutenylcarbinol,

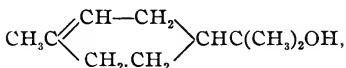


and ethylallylisopropenylmethane,

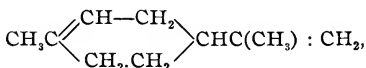
¹ J. Chem. Soc., 87, 639, 655 (1905).



the object being to compare their properties with those of terpineol,

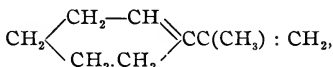


and dipentene,

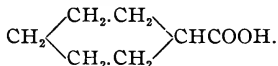


respectively. The conclusion is drawn that, although the open chain compounds show certain similarities in behavior to the terpenes and their derivatives, yet the closed chain structure has a distinct influence on the properties of the terpenes.

In his next paper¹ a description is given of the synthesis of a number of terpenes such as $\Delta^{3,8(9)}$ —normenthadiene,



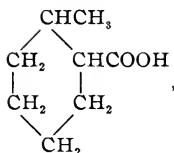
which do not contain the paramethyl group that is so characteristic of the natural terpenes. The starting point in the synthesis was hexahydrobenzoic acid,



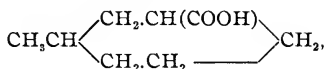
It is well known that the natural terpenes and allied compounds are almost exclusively derivatives of paracymene, or are easily converted into such derivatives. In the last two papers² of the series under consideration, the synthesis of terpenes derived from orthocymene and from metacymene is described. In general properties these resemble the para compounds. The starting points for the preparations were *trans*-hexahydroorthotoluic acid,

¹ J. Chem. Soc., 87, 661 (1905).

² *Ibid.*, 87, 1066, 1083 (1905).

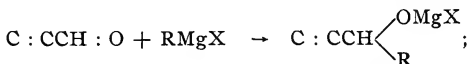


and hexahydrometatoluic acid,

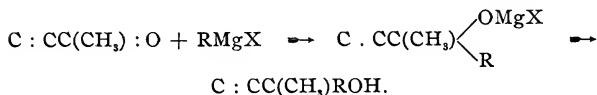


respectively, the methods and reactions being similar to those described in the earlier portion of this report (p. 90).

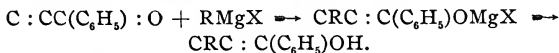
In a series of interesting papers¹ on the reaction of alkyl magnesium halides with various unsaturated compounds. Kohler and his fellow workers have discovered the following regularities: (1) The magnesium derivative invariably adds itself to the carbonyl group of unsaturated aldehydes,



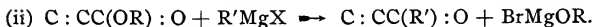
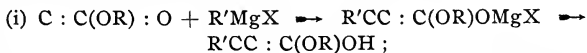
this gives, ultimately, the carbinol $\text{C} : \text{CCHROH}$. (2) Unsaturated ketones containing the group CH_3CO react like aldehydes,



(3) Unsaturated ketones containing the group $\text{C}_6\text{H}_5\text{CO}$ add the magnesium reagent in the positions 1,4,



(4) The esters of unsaturated acids react both by 1,4 addition and by the replacement of alkyloxyl by alkyl:



¹ THIS JOURNAL, 31, 643; 33, 21, 35, 153, 333; 34, 132, 570.

The first equation represents the principal reaction of aromatic magnesium compounds with such esters, the second that of aliphatic magnesium compounds, but the result is also somewhat dependent on the nature of the atoms or groups in the α -position to the carbonyl, negative groups increase the extent of the additive action.

See report V.37 p. 68
The application of the Grignard reaction has received further extensions by three noteworthy improvements in its technique. The earlier users of the Grignard reagent regarded the ether which was employed in its preparation as being merely an indifferent solvent, but it was speedily recognized, by Grignard himself¹ and also by Blaise,² that the reaction between magnesium and the alkyl haloid would not take place in the absence of ether; the latter was, therefore, assumed to be present in the resulting compound as "ether of crystallization." W. Tschelchizeff³ has carried out a series of experiments which show that, although alkyl haloids and magnesium do not react in the absence of ether at the temperatures usually employed, they will do so at higher ones, for instance in vigorously boiling benzene, or better, in toluene solution. The ether, therefore, acts simply as a typical catalytic agent and an extremely small amount of it is sufficient to bring about the formation of the Grignard reagent at the ordinary temperature. It thus becomes possible to prepare the reagent and carry out the subsequent reaction in a solvent other than ether, whereby the upward limit of temperature which may be employed is raised. The same author had shown, in a previous paper,⁴ that a tertiary base, such as dimethylaniline, could take the place of the ether in the Grignard synthesis and that, in some cases, such a substitution was of practical advantage. In a later paper⁵ he records the results of his determination of the "heats of formation" of a number of Grignard reagents from ether and various organomagnesium halides. The experiments were carried out by mixing magnesium powder with excess of the alkyl haloid, adding a neutral solvent, usually benzene, and then a few drops of dimethylaniline to act as a catalyst; when the reaction was completed a known excess of ether was poured in and the resulting evolution of heat was measured. These experiments, as well as his previous work, lead the author to the conclusion that Grignard's reagent is an oxonium compound, as suggested by Baeyer and Villiger,⁶

¹ Dissertation, University of Lyons, 1901.

² Compt. rend., 132, 839.

³ Ber. d. chem. Ges., 38, 4534 (1904).

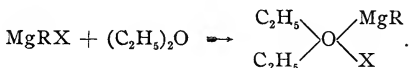
⁴ *Ibid.*, 37, 2081 (1904).

⁵ *Ibid.*, 38, 3664 (1905).

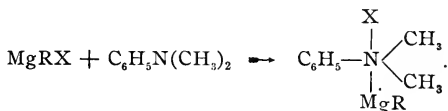
⁶ *Ibid.*, 35, 1201 (1902).

see errata
V.37 p. 68!

and that its formation is represented by the following equations:



The reaction is, of course, similar if a tertiary base such as dimethylaniline, is employed instead of ether,



In the course of their investigations of triphenylcarbinol derivatives, Baeyer and Villiger¹ were unable to obtain magnesium derivatives of brom- or iodoaniline or of the corresponding dimethylanilines. Sachs and Ehrlich,² who had encountered the same difficulty, overcame it, to some extent, by treating the magnesium with ethyl bromide then, as soon as the reaction was well started, the greater portion of the liquid was poured away and parabromdimethylaniline was added; under these circumstances a small portion of dimethylaniline-magnesium bromide was formed which proved to be sufficient for their qualitative purposes, though it was, of course, contaminated with other substances and was unsuited for the preparation of pure derivatives. Baeyer continued his work on the subject and has recently described an extremely simple and beautiful method for the preparation of a highly reactive form of magnesium.³ Magnesium filings are heated in a flask and half their weight of iodine added gradually. The product forms a dull gray powder, which acts with great energy on water and on methyl alcohol, hydrogen being evolved and magnesium hydroxide and methoxide, supposedly, being formed. The action of ethyl alcohol is feebler and amyl alcohol has no effect on the magnesium compound. The nature of this magnesium halide is not stated, but it is, presumably, a subiodide, possibly similar in composition to Cd_4I_7 .⁴ At all events it differs markedly in properties from the normal anhydrous magnesium iodide.

The magnesium subiodide is without action on chlor-

¹ Ber. d. chem. Ges., **36**, 2775 (1903).

² *Ibid.*, **36**, 4296 (1903).

³ *Ibid.*, **38**, 2759 (1905).

⁴ Morse and Jones: *THIS JOURNAL*, **12**, 491 (1890).

benzene, but it acts energetically on brombenzene and on all the iodoanilines and dimethylanilines, most readily with the ortho derivatives, least so with the para compounds. The use of this reagent has already permitted the preparation of all the possible aminotriphenylcarbinols and there can be no doubt that its employment will prove to be extremely useful in other directions. Although, in the preceding pages, reference has been made to some only of the more interesting points which have been developed recently in connection with Grignard's reaction, sufficient evidence has, perhaps, been offered, to demonstrate that this most fruitful and admirable synthetical method still maintains its popularity and that the results obtained by its use show no diminution in their interest and value.

J. BISHOP TINGLE.

REVIEWS.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D., Associate Professor of Industrial Chemistry in the Massachusetts Institute of Technology. New York : Macmillan Co. 1905. Price, \$3.50.

Reviews by Professor Mallett of the previous editions of this work have been published in this JOURNAL.¹ It is only necessary to say that the present edition is enlarged, improved and thoroughly revised, and that the author has added an outline of elementary metallurgy ; we consider this edition of Professor Thorp's work a very valuable text-book.

E. R.

A TEXT-BOOK OF CHEMICAL ARITHMETIC. By HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. First Edition. First Thousand. New York : John Wiley and Sons. 1905. 12mo. vii + 169 pages. Price, \$1.25.

This is an excellent book for students of quantitative analysis, for whom it is intended, but it will also be found very useful for beginners. The use of the methods of abbreviated multiplication and division will save much time and many errors.

E. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1905. NOUVEAUX APPAREILS DE LABORATOIRES, MÉTHODES NOUVELLES DE RECHERCHES APPLIQUÉES À LA SCIENCE ET À L'INDUSTRIE. Avec 180 figures. By CAMILLE POULENC, Docteur des Sciences. Paris : J. B. Ballière et Fils. 1905.

In this, as in the preceding volumes of the series, M. Poulenec gives an illustrated list of all new apparatus and new methods.

¹ THIS JOURNAL, 21, 181 ; 23, 268.

Much of the apparatus of course is trivial or of doubtful utility, but many useful improvements are described. Some of the methods given in detail are of absorbing interest, such as the methods and apparatus of M. and Mme. Curie for the study of radioactive substances; M. Verneuil's apparatus for the manufacture of artificial ruby; Moissan and Rigaut's apparatus for preparing pure argon; and Wachsmuth's apparatus for determining acoustically the density of gases and vapors.

E. R.

see errata p. 570

DIE NEUEREN ENTWICKELUNG DER KRISTALLOGRAPHIE. Von DR. H. BAUNHAUER. Braunschweig: Fr. Vieweg u Sohn. 1905. pp. 184. Price, M. 4.

The seventh of the Natural History monographs issued by Vieweg und Sohn is an excellent example of the "digestive" works which this series aims to supply. The present volume, though not exhaustive, is complete and well balanced. It is also up-to-date in its discussions of various problems presented by crystallography. It gives a clear, succinct account of the fundamentals of the science, among which it emphasizes the Law of Zones and the Rationality of the Indices. The treatment of geometrical crystallography is good, giving in an orderly but individual way the characteristics of the symmetry properties and crystal classes now recognized by all crystallographers. The means employed for determining the symmetry of crystalline bodies are well described, and the newer work on the formation of twins and crystal growth is well summarized.

Towards the end of the book the author devotes twenty or more pages to the less established conclusions of chemical crystallography. Here the treatment changes from the broader conclusions generally accepted to the conclusions of individual workers and the more specific cases. There is an evident attempt to maintain the same attitude throughout, but the uncertainty in this newer field of investigation is clearly manifest. The relations existing between chemical constitution and crystal structure are hinted at by reference to the fact that compounds like Fe_2O_3 , FeCl_3 , or $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, show trigonal or hexagonal symmetry while ZrSiO_4 , $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and others are tetragonal. It is, however, manifestly too early to draw serious conclusions on these problems.

The book is unusually good in its place. It is not a textbook for the beginner, nor a treatise for the advanced student, but for those who have some knowledge of crystallography and wish to keep abreast of the advances made in that science it can hardly be excelled.

EDWARD B. MATHEWS.

A TREATISE ON CHEMISTRY. BY SIR H. E. ROSCOE, F.R.S., AND C. SCHORLEMMER, F.R.S. Volume I. The Non-Metallic Elements. New edition completely revised by Sir H. E. Roscoe assisted by Drs. H. G. Coleman and A. Harden, with 217 illustrations and a portrait of Dalton engraved by C. H. Jeens. London and New York : Macmillan & Co. 1905. pp. 931.

The new edition of "Roscoe and Schorlemmer" is of special interest to chemists at the present time, for with the exception of Dammer's "Handbuch," which has a supplementary volume reporting progress up to 1903, there is no large manual, in English, French or German at least, which includes the work of the past ten years in inorganic chemistry ; there is an abundance of new small text-books, of which Erdmann's is the largest and most thorough, but no book to which the student can turn for reference excepting Dammer's "Handbuch," which is simply a reference-dictionary and not a treatise of chemistry. Hence the present volume is especially welcome, and it is to be hoped that the one on the metals will appear soon.

Roscoe's manual has a definite place among the other large text-books. While it is not as exhaustive in treatment as Graham-Otto, it mentions every well-authenticated inorganic compound, and gives the more important references to literature. All new technical methods in use occupy sufficient space, and chemical theory, old and new, finds place as well ; but the book is distinctly a descriptive rather than a theoretical treatise. Above all it is not too large to study with profit, while it is comprehensive enough to serve as a reference book in most cases.

The new edition is quite up-to-date, as a few examples will show. It includes Baeyer and Villiger's work on hydrogen peroxide and the persulphuric acids ; the work of Bone, Lewes and Smithells on flame and the combustion of hydrocarbons ; of Dixon on the phenomena of explosion ; of Ramsay, Travers and Soddy on the rare gaseous elements in the air and on helium. It gives a full description, with drawings, of the improved processes for making coal gas, with due attention to oil gas, wood gas, water gas, acetylene and the different fuel gases ; it describes the various contact processes for the manufacture of sulphuric acid ; the electrolytic methods of making chlorine and hydrochloric acid ; the manufacture of nitric acid from Chili saltpeter, from ammonia by Ostwald's process, from the air by Bradley and Lovejoy's process.

To praise further "Roscoe and Schorlemmer" is superfluous, as it has established its place in the esteem of chemists. It is enough to say that Sir Henry Roscoe and his coworkers, Dr. Coleman and Dr. Harden, have performed the task of revision with great ability. It is scarcely necessary to add that the publishers have printed and illustrated the book faultlessly.

E. R.

AMERICAN CHEMICAL JOURNAL

THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES.

BY ROGER CLARK WELLS.

In a recent paper upon the nephelometer,¹ a perfected form of this instrument was described and shown to be well fitted for comparing the scanty precipitates usually called opalescences. By the use of prisms the precipitates in two test tubes could be viewed in one field of vision and an accuracy of about 1 per cent was attained in the comparison of nearly equal opalescences. The nephelometer would appear to be a better arrangement than that described by Tswett,² because the light strikes the tube sidewise, and one can view the whole tube, instead of looking across the tube through which a pencil of light is passed. Some illustrations of the method of estimating chloride in an unknown solution were given and some general precautions mentioned, but a detailed discussion of the phenomena of opalescent precipitates was reserved for a future paper. During the frequent use of the nephelometer in the revision of the atomic weight of sodium and chlorine,³ the meth-

¹ Richards and Wells: *THIS JOURNAL*, **31**, 235 (1904).

² *Z. physik. Chem.*, **36**, 450 (1901).

³ Richards and Wells: *J. Am. Chem. Soc.*, **27**, 484 (1905).

ods of nephelometry were studied and improved until they were sufficiently accurate for the special ends in view. Among the facts which remained to be investigated more thoroughly, however, was the variation of opalescence with time. The present paper contains an account of experiments made upon this subject, as well as upon a great many other points which will widen the range of applicability of nephelometric methods.

Silver chloride is a very suitable salt for studying these questions. Its solubility is small in the ordinary sense, yet large as measured by the nephelometer. The presence of other salts or acids up to concentrations of about $N/0.01$ does not alter its solubility or at most, only very slightly. In accordance with our present theories of solution the dissolved silver chloride is, on account of the great dilution, completely ionized and there will be, in general, a concentration of silver and a concentration of chloride which will be equal for only one special case. Moreover, it appears to fulfil the demands of the concentration law (mass law) surprisingly well, for a solution of it can be practically freed from chloride by the addition of sufficient ionized silver and from silver by the addition of ionized chlorine.

The difficulty, in previous work, was the selection of the major variables and the control of these so that only one might be varied at a time. This was a hard problem as long as two tubes were compared with each other, for one could not decide whether the observed relative variation was due wholly to the first, partly to the first and second, or wholly to the second tube. The results of this paper would not have been attained if a constant standard of reference had not been found. At first suspensions of chalk were tried,¹ but they proved even more variable than the opalescences. Ground glass, however, appeared to be well adapted to the purpose. Ordinary window glass (plate glass might have been better) was cut into pieces about an inch square and these were ground by fine emery until a series was obtained which ranged from opacity to transparency. Some were ground on both sides. All were covered by black paper having a round hole in the center about 16 mm.

¹ Ostwald-Luther, "Physico-chemische Messungen," p. 248.

in diameter. When such a plate was placed upon the top of the sliding tube in the nephelometer, in a definite and reproducible position, it had exactly the appearance of an opalescent precipitate. The slight color of the window glass only heightened the resemblance. Nearly all the results in this paper, then, were obtained by comparing a single tube of opalescence with a standard glass, and it is evident that the results so obtained are more reliable than the observations published heretofore. Several of the glasses were standardized, after the needful precautions had been learned. For example, one was found by about 20 trials to be equivalent to 15.1 arbitrary units of opalescence, the extremes being 10 and 19. At first sight this does not appear to be at all accurate, but when one reflects that, under improper conditions, the readings might be as high as 45, it appears more satisfactory.

With a constant standard of reference the effect of a great many variations might have been studied. What proved to be major variables proved also to be dependent upon each other. Some of the most obvious influences are the manner of precipitating and stirring the solution. These operations were done as uniformly as possible in all the experiments. Whenever definite, very dilute solutions were prepared, by diluting more concentrated ones, or whenever small quantities of electrolytes were added, the solutions were stirred most thoroughly, and finally allowed to stand for a few minutes to make them still more uniform. During precipitation, also, they were stirred thoroughly and uniformly, usually 20 strokes, with the propeller-shaped platinum stirrers, previously described. More than 20 strokes had no further effect. Failure to stir when precipitation begins results in a noticeable alteration of the intensity of opalescence. Uniform precipitation seems to be hard to attain, but perhaps it might be regulated somewhat by using just the right concentration of precipitant. As regards light, most of these experiments were done in the dim light of a single 16-candle-power light in a dark room. Some were repeated in red light alone, but no difference was detected. When not under direct observation, all tubes stood in a box in absolute darkness. Of course the opalescences darken in day-

light, but no darkening was ever certainly proved to be due to the light of the room in which experiments were performed. Even some weak opalescences exposed to the light of the nephelometer for 2 hours were not darkened perceptibly.

The silver nitrate employed had been sufficiently recrystallized to free it wholly from chloride. The potassium chloride had been purified by precipitation with hydrochloric acid. The nitric acid used had required three wasteful, fractional distillations before it was free from chloride. The potassium nitrate had been evaporated to dryness with the addition of nitric acid until all hydrochloric acid was expelled; it was then recrystallized from water. The sulphuric acid was boiled. Aluminum nitrate was prepared by dissolving clean strips of the metal in the pure nitric acid. Throughout the work great precautions were taken to get rid of contaminating chlorides from the air, the desk and the hands. It is a pleasure to thank Mr. William D. Hutchinson, of Oxford University, for his kind assistance in preparing some of the standard solutions and in making a number of the preliminary observations.

1. Effect of the Medium in which Precipitation Occurs.

When silver chloride is precipitated by mixing fairly concentrated solutions, large curds settle out and very little opalescence is observed. In more dilute solutions, about normal for example, the addition of a silver salt to a chloride leaves a marked opalescence, but, strange to say, the addition of chloride to the silver salt results in a coagulation and, consequently, much less opalescence. Ionized silver, therefore, appears to have marked coagulating power since it is present in excess during precipitation in the latter case. Precipitation from extremely dilute solutions yields a fine state of division or suspension. This coagulates or clarifies slowly upon shaking, much faster in the presence of nitric acid. Similarly, during repeated washings of the precipitate in pure water it tends to go into an emulsion or milky state, which will not clear for days, alone, but usually clarifies by the addition of nitric acid. Now nitric acid has been shown to hasten the development of opalescent precipitates also and one may thus infer that pre-

precipitation and coagulation are very closely related. Indeed, it is impossible to draw any line between the two phenomena—precipitation must be a process of coagulation. The object of the nephelometric experiments was, therefore, to attain this coagulation in a definite and reproducible fashion. It appeared reasonable to suppose that the maximum opalescence which could be attained in any way would most nearly represent the truth. For practical purposes the quickest way to attain that maximum would also be desirable. Hence, it might appear that all experiments should record a study of the speed of precipitation. They should, were it not for the fact that opalescences forming at different rates, in different media, do not, necessarily, attain the same intensity. Very slow precipitations appear, in general, to be swamped by superimposed effects, so that they never attain the maxima which quickly forming opalescences acquire. The variable to be controlled first in nephelometric observations, therefore, is the medium. In order to point out the effect of various media, the maximum opalescences which could be attained, without regard to the time required to attain the maximum, are here stated. Then, under a separate head, will be shown the speeds attained in the best media.

Intense Opalescences.

KCl (N/o.000040) precipitated by AgNO_3 .

	Intensity of opalescence.
In water	21 ¹
N/o.05 HNO_3	29
N/o.05 $\text{Al}(\text{NO}_3)_3$	29
N/o.025 KNO_3	32

AgNO_3 (N/o.000040) precipitated by KCl.

	Opalescence.
Without any electrolyte	21
In N/o.025 $\text{Al}(\text{NO}_3)_3$	16
In dilute H_2SO_4	28
In N/o.025 HNO_3	30
In N/o.025 KNO_3	31
In $\text{HNO}_3 + \text{KNO}_3$	26
In $\text{HC}_2\text{H}_3\text{O}_2$	24

¹ These numbers are merely the reciprocals of the heights of opalescence appearing equal to a glass, multiplied by 1000. They indicate intensity of opalescence on an arbitrary scale.

The opalescence in water alone would probably not have been so great if the traces of electrolyte produced by metathesis could have been eliminated. Hence the presence of electrolytes appears advantageous in these intense opalescences.

Weak Opalescences.

KCl (N/o.000007) precipitated by AgNO_3 .

In the first experiments about a drop of fairly concentrated solutions of various salts was added to each tube. Tubes without any electrolyte attained the greatest opalescence. This was attributed to a possible greater solubility of silver chloride in the solutions containing electrolytes. It may be related to the coagulative power of ionized silver. With only traces of electrolytes, all the tubes behaved similarly. Further experiments might well be made on this case, with special regard to the proper excesses required, according to the results shown later.

AgNO_3 (N/o.0000040) precipitated by KCl.

	Opalescence.
In water	14
In N/o.025 KNO_3	20
In N/o.025 $\text{Al}(\text{NO}_3)_3$	18
In N/o.025 HNO_3	18
In trace of HNO_3	18

A different glass was used for weak opalescences than for intense opalescences. In this case electrolytes appear to be advantageous, as usual.

Experiments were also made with "actual" silver chloride solutions. The phenomena were, in general, similar to the above, except for time effects to be noted later. No better electrolytes than potassium nitrate and nitric acid for intensifying opalescence were found. The quantity to be used depends upon the amount of precipitate; it should be small with slight quantities of precipitate.

It is believed that the excesses used for precipitation in the cases above were sufficient. A full study of that matter had not been made when these results were obtained and hence

less attention was paid to it. Below are given the results bearing upon that particular question.

2. *The Excess Required to Produce Maximum Opalescence.*

This point has been frequently discussed. Mulder thought that four times the equivalent of soluble salt was required of the precipitant to insure complete precipitation from silver chloride solutions. Stas considered a threefold excess sufficient. Several workers have pointed out that the earlier conclusions varied according to the means used to detect the opalescence.¹ Without regard to theories, experiments were made upon this point.

KCl (N/0.000040) precipitated by AgNO₃.

					Intensity of opalescence.	
Excess	5 times equivalent of KCl				31 } 29 }	30
"	10	"	"	"	25 } 33 }	
"	100	"	"	"		29
"	1000	"	"	"		24
"	10000	"	"	"		18

Although any excess of silver nitrate up to 100 times the equivalent of potassium chloride causes no appreciable variation of the opalescence, an excess of 1000 times causes a diminution. This may be due to the great coagulative power of ionized silver, or, more likely, to the formation of a soluble double salt.

AgNO₃ (N/0.000040) precipitated by KCl.

Excess	5 times equivalent of AgNO ₃					Intensity of opalescence.
						23
					26	26
"	10	"	"	"	29	
					24	
					23	
					30	
"	50	"	"	"	"	31
"	200	"	"	"	"	32
"	300	"	"	"	"	22
"	1000	"	"	"	"	28
					27	28

¹ Hoitsema; Z. physik. Chem., 20, 272 (1896). Richards and Wells; J. Am. Chem. Soc., 27, 483 (1905).

The variation of opalescence with excess is here hardly beyond the limit of error of single observations. Certainly a large excess produces no appreciable diminution of opalescence. The two preceding solutions were very concentrated in comparison with real silver chloride solutions, hence more dilute ones were next investigated.

With very dilute solutions, about $N/0.000004$ and small excesses, a phenomenon like supersaturation was apparent. Excesses of 8 times usually failed to produce an opalescence, but excesses of 10 times caused a faint opalescence. Here was illustrated the requirement that the solubility product must be exceeded before precipitation can occur. When the solubility product was barely exceeded, opalescence could be made to appear by vigorous stirring. Thus supersaturation does not appear to be limited to soluble salts and there is no reason to suppose that it should be; but it required rather delicate regulation of the concentrations to render it visible in the case of silver chloride. The influence of the medium was very marked. Only results obtained in proper media are given below, the variations for pure water being enormous; in every case where variation with time was observed the maximum is recorded.

KCl ($N/0.0000040$) precipitated by $AgNO_3$.

						Opalescence.
Excess	25	times	equivalent	of KCl		
"	75	"	"	" KNO_3	20	} 24
"	75	"	"	" HNO_3	24	
"	75	"	"	" both	29	
"	225	"	"	" KCl	25	} 30
"	450	"	"	" "	33	
						24

Here the result of too small an excess is very marked, but the diminution caused by a large excess is small, if any.

AgNO_3 (N/o.0000040) precipitated by KCl.

Excess	15-fold	KNO_3	50 min.		Opalescence.
"	25	"	HNO_3 40 "	17	14
"	25	"	KNO_3 50 "	18	20
"	25	"	HNO_3 4 hours	26	
"	50	"	KNO_3 40 min.	26	24
"	50	"	HNO_3 40 "	21	
"	60	"	" 50 "	26	27
"	60	"	both 50 "	27	
"	75	"	" 3 hours		31
"	100	"	KNO_3 40 min.	20	24
"	100	"	HNO_3 40 "	30	
"	100	"	" 2 hours	22	18
"	200	"	" 10 min.		

Notwithstanding the variations which occurred with different media and in the times at which the maxima were observed, a decided regularity is apparent. The maximum opalescence occurs with an excess of about 70 times the equivalent of the ionized silver to be precipitated. If this is more than the theory requires it is probably due to an overcoming of the tendency towards solubility of the silver chloride in the media employed.

The phenomena for medium concentrations undoubtedly lie between the two extremes of N/o.00004 and N/o.000004 studied.

8. The Time Required to Obtain Maximum Opalescence.

The speed of opalescent precipitation is affected by many interrelated variables. For example, it depends upon the excess used, although the influence is not great, providing a proper excess has been used. As one would expect, the greater excess was found to cause a quicker precipitation. Silver nitrate (N/o.000004) was precipitated in two similar solutions containing nitric acid, with opalescence as follows:

Time. Minutes.	Excess 25 times.	Excess 100 times.
10	18	21
50	20	22
540	22	21

The speed is, undoubtedly, affected by temperature. No

experiments were made to illustrate this point, since the tubes which were being compared were usually at the same temperature. The room also remained fairly constant in temperature. This question should receive attention if a method of estimation by standard glasses is perfected, so that corrections could be made for readings taken at different temperatures.

For practical purposes of nephelometry the object is to attain the maximum opalescence in the shortest time possible. The accelerating influence of certain electrolytes had been previously pointed out in a qualitative way.¹ It seemed wise, therefore, to study the specific influence of a number of new electrolytes, following the precipitation in a quantitative way by reference to constant glasses. Below are given some of the results so obtained.

AgNO_3 (N/o.000040) precipitated by KCl (10-fold excess.)

Time.	Without addition of any salt.	In $\text{N}/0.025$ KNO_3 (trace of HNO_3).	$\text{KNO}_3 + \text{HNO}_3$.	HNO_3 .	Trace HNO_3 .	$\text{Al}(\text{NO}_3)_3$ (trace HNO_3).	Dilute H_2SO_4 .	Trace H_2SO_4 .	$\text{C}_2\text{H}_4\text{O}_2$.
Opalescences.									
1 min.	8	25	16	15	11	14	9	8	7
15 "	9	31	26	30	13	16	.	.	10
30 "	10	29	23	29	14	15	28	13	.
80 "	14	28	20	28	14	16	27	19	21
4 hrs.	20	24	21	26	17	16	26	24	23
14 "	21	18	18	24	16	16	23	.	24

It will be noticed that the tube containing potassium nitrate attains maximum opalescence in 15 or 20 minutes. Next in order of speed follow the tubes containing nitric acid, potassium nitrate plus nitric acid, and sulphuric acid. The tube without any electrolyte except that added to precipitate or that produced by metathesis was still increasing slowly at the end of 14 hours. The results were not always so without electrolytes, however, as was shown when considering the medium under the head, weak opalescences.

Such readings, extending over many hours, were made with

¹ Richards and Wells: J. Am. Chem. Soc., 27, 486 (1905).

intense, medium and weak opalescences when precipitated by the addition of silver nitrate to potassium chloride, potassium chloride to silver nitrate and each of these salts to actual solutions of silver chloride, in the presence of the various electrolytes above mentioned, about 400 observations in all. The publication of these readings would require many pages. Since many of them turned out to be mere repetitions it seems wiser to state only the general conclusions.

In general, the substances which aid in producing maximum opalescence also hasten the speed of its formation. Hence, the behavior in water alone was exceptional in every case, except that of the very weakest opalescences. No better accelerators than the "strong electrolytes," salts and the mineral acids, were found. The time of maximum opalescence with good accelerators present varied for the different cases, roughly as follows:

Intense opalescences (about $N/0.00005$).

				Time of maximum. Minutes.
AgNO ₃	added to	KCl		4
"	"	"	AgCl	20
KCl	"	"	AgNO ₃	30
"	"	"	AgCl	20

Medium opalescences (about $N/0.00002$).

				Time of maximum. Minutes.
AgNO ₃	added to	KCl		10
"	"	"	AgCl	25
KCl	"	"	AgNO ₃	25
"	"	"	AgCl	25

Weak opalescences (about $N/0.000005$).

				Time of maximum. Minutes.
AgNO ₃	added to	KCl		20
"	"	"	AgCl	30
KCl	"	"	AgNO ₃	30
"	"	"	AgCl	30

In practice it was so difficult to control all but one variable that the results above have a relative rather than an absolute significance. Particularly, too much significance must not be

attached to the times, 30 minutes and over, for the opalescence had, in those cases, become so stable that it usually varied only slightly for 3 or 4 hours further, and the exact maximum fell now at one time, now at another. On this account, if the most exact results are desired, observations should always continue until opalescence begins to fade. Only in this way can one be absolutely certain that the maximum has been attained. That these insignificant variations were due to the state of the water or temperature is rendered probable by the fact that, when the maximum was late in its attainment in one case it was late in the other tubes that day.

Perhaps the most striking fact in the results is that "actual" silver chloride solutions attain their maximum so much more uniformly than chlorides or silver salts precipitated by the opposite ion. These facts bear upon atomic weight work. In the equal opalescence method, with chloride, the time of observation need not be extended beyond an hour, although no error would be introduced by so doing. In determining chloride in a silver chloride solution, however, by nephelometric methods, this point would have to be considered. The proper procedure would be to precipitate the unknown silver chloride solution, allowing it to develop for 16 minutes, then to precipitate the standard solution and make the comparison at the end of the next 4 minutes. The time would be somewhat differently adjusted if silver were being determined. But the use of a glass as a standard of reference would be the best way of all.

A small correction may now be made for this error in determining the atomic weight of sodium. Since the unknown opalescence attained its maximum after the known had begun to fade, too much standard solution was used to match, finally, the unknown opalescence; hence the soluble chloride recorded was too great. The error so committed might have amounted to 20 per cent in the solubility, therefore about 0.002 per cent in a usual determination, hence 0.001 unit in the atomic weight of sodium. The result attained by the gravimetric method, 23.006 (if $\text{Ag} = 107.93$), would become 23.007 with this correction, therefore, but the final average with the result of the equal opalescence method, 23.009, would still remain 23.008.

It is also now very clear why, in the earlier work with the nephelometer, the ratio of two tubes occasionally changed enormously with time,¹ for the standard was increasing in intensity, the unknown solution decreasing. This is shown by the following example :

Time.	Ratio of opalescences.
5 min.	3.20
15 "	2.76
30 "	2.20
60 "	1.59
2.5 hours	1.19
7 "	1.08
15 "	0.99

It also becomes interesting to speculate as to the causes of the ever shifting opalescences. It is evident that a given number of small, separate, visible particles will cause a greater opalescence than the same number collected into an aggregation, for the reflecting surface exposed will be greater. But if it be assumed that some of the single particles are too small to reflect light at all, that would not be true. As the latter assumption is a likely one, the development of opalescence is probably due to aggregation, and precipitation is only the point where the aggregations first attain the limit of visibility. The aggregation may be hastened initially by the presence of electrolytes. The action has been variously explained; Whetham shows agreement between the facts and the theory that a certain number of electrostatic charges must be brought within reach of a colloidal group.² Hence, he assumes that coagulation occurs in consequence of a change in the surface energy of the colloids, due to the presence of the electrostatic charge. Quincke explains the phenomena solely by surface tension changes. It seems reasonable to suppose that aggregation could only be expected to occur rapidly while the particles are small and their kinetic motion or diffusion is rapid. As aggregations become larger the process will become slower, until a point is reached where all aggregations have attained the

¹ J. Am. Chem. Soc., 27, 484. Many results attained in the earlier work appeared so anomalous that they were never published.

² "A Treatise on the Theory of Solution," p. 396 (1902).

limit of visibility and the exposed surface, and therefore the opalescence, begins to decrease, owing to further aggregation. The decrease is less dependent upon the medium than is the initial formation of opalescence. Moreover, a small part of the decrease is due to settling of the particles under the influence of gravity.

The above suppositions are very closely related to the present theories of colloids, and the peculiar behavior of silver chloride has previously been ascribed to its colloidal condition.¹ But Picton and Linder have pointed out that there is probably no difference in kind between a colloid and a crystalloid.² This is made especially clear by Beckhold in a paper upon the agglutination of bacteria.³ He points out that is a continuous transition from crystalloids in the first place to those bodies, partly colloidal, which aggregate in solution so as to produce high molecular weight, then to the real colloids, which look like solutions but are really suspensions and, finally, to the visible suspensions. Many colloids are coagulated by the addition of univalent, bivalent and trivalent salts with the relative speeds, 1 : 35 : 1023.⁴ The action of aluminum nitrate was tried for the purpose of seeing if silver chloride belongs to this class. Since aluminum nitrate had no unusual effect, two possibilities remained. Either silver chloride is not a colloid, or else it is one which moves with an electric current and hence, according to Hardy,⁵ one would expect only anions to affect its coagulation. Without knowing about its movement in an electric field, coagulation in the presence of sulphates was tried. These also failed to cause unusual speed of coagulation. Hence, there remained only one argument in favor of the colloid theory, the occasional color of the opalescences. This, however, can be accounted for by strictly physical conceptions. The only tints appearing were a pale blue or a faint reddish-brown; now Lord Rayleigh has shown that when the size of

¹ Richards and Wells: *J. Am. Chem. Soc.*, **27**, 484.

² *J. Chem. Soc.*, **61**, 148 (1892).

³ *Z. physik. Chem.*, **48**, 385 (1904).

⁴ Schulze: *J. prakt. Chem.*, **25**, 431 (1882).

⁵ *P. Roy. Soc.*, **66**, 110 (1900).

reflecting particles approaches the wave length of light they begin to cease reflecting ; but the short blue waves are reflected by particles small enough to transmit the red waves. It seems probable, then, that opalescences occasionally appear blue for the same reason that the sky does,—the smallness of the reflecting particles. Similarly, the red tints would be accounted for by transmitted light which has lost its blue component by partial dispersion, though these were not so frequently observed as the blue tints.

It is also interesting to notice that many of the phenomena studied in this paper have a direct bearing upon photography. During the ripening of plates the change of powdery to granular silver chloride takes place. Eder records that unripe emulsions show the red and blue tints by transmitted light.¹ According to Liesegang the presence of potassium bromide in developers increases the size of the granules of silver,² but this is just what would be expected in accordance with the results of the nephelometer.

4. *Proper Treatment for Estimating Various Opalescences.*

In order to save the time of those attempting nephelometry, the precautions for several typical cases are here collected :

Intense Opalescences (N/0.00005) :

Silver nitrate added to potassium chloride : Add nitric acid or potassium nitrate. Use 8-fold excess. Read in 4 minutes.

Silver nitrate added to silver chloride already containing potassium nitrate. Read in 20 minutes.

Potassium chloride added to silver nitrate : Add electrolyte. Use 50-fold excess. Read in 30 minutes.

Potassium chloride added to silver chloride, already containing potassium nitrate. Read in 20 minutes.

Weak Opalescences (N/0.000005) :

Silver nitrate added to potassium chloride : Add electrolyte. Use 100-fold excess. Read in 20 minutes.

Silver nitrate added to silver chloride, already containing electrolyte. Read in 30 minutes.

¹ "Photographie," 9, 66 (1902).

² *Loc. cit.*, p. 102.

Potassium chloride added to silver nitrate: Add electrolyte. Use 70-fold excess. Read in 30 minutes.

Potassium chloride added to silver chloride, already containing electrolyte. Read in 30 minutes.

In general, therefore, the object is to make the standard tubes as nearly like the unknown as possible, or, if standard glasses are being used, to attain the maximum.

The question naturally arises whether the forced maxima are really as uniform as less intense opalescences attained after repose. A considerable weight of confirmatory evidence, which will appear shortly in another paper, shows, conclusively, that the maxima are the best measures of the concentration. Moreover, electrolytes must be present in some solutions and uniformity, therefore, demands that they be present in all. It is very likely that, occasionally, an extreme maximum will be produced, just as too weak opalescences may occur; hence the average of several observations will approach nearer the truth than only one or two.

Summary.

1. The chief sources of error in previous nephelometric work are pointed out.
2. The use of ground glass standards of reference proved advantageous in studying the variation of opalescent precipitates with time.
3. For every concentration a suitable medium and excess of precipitant is required.
4. Electrolytes both augment the maximum opalescence to be precipitated from a solution and hasten its deposition.
5. The bearing of these facts upon other fields is pointed out.
6. Directions for procedure are given for several special cases of nephelometry.

CHEMICAL LABORATORIES,
HARVARD COLLEGE AND
UNIVERSITY OF PENNSYLVANIA, 1905.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE BEHAVIOR OF BENZOYL CARBINOL TOWARDS ALKALIES AND OXIDIZING AGENTS.

BY WM. LLOYD EVANS.

Zincke and his students were the first to study the behavior of benzoyl carbinol towards oxidizing agents.¹ They found that it gives, according to the oxidizing agent used, varying proportions of mandelic, benzoylformic, benzoic and carbonic acids. The most notable of their experiments was the action of copper and sodium hydroxides on benzoyl carbinol and acetolacetate, *r*-mandelic and *r*-lactic acids, respectively, being the chief reaction products obtained. Zincke suggested² that in this reaction the benzoyl carbinol might first be resolved into benzaldehyde and formaldehyde and that these products might subsequently combine to give *r*-mandelic aldehyde, whose conversion to the corresponding acid, in the presence of the oxidizing agent, would then be readily understood. He also presented the view that the aldehyde of benzoyl carbinol might first be formed by direct oxidation of the primary alcohol group present in benzoyl carbinol and that the resulting benzoylformaldehyde might be converted to mandelic acid by intramolecular oxidation and reduction,³



Kling, in his recently published statement,⁴ divides the action of oxidizing agents into three categories, according to the relative amount of lactic, acetic and carbonic acids obtained from the analogous acetyl carbinol.

It is clearly evident from the work of Nef⁵ that mandelic and lactic aldehydes cannot be isolated as such, but are transformed spontaneously into the isomeric benzoyl and acetyl

¹ Ber. d. chem. Ges., **13**, 635. Ann. Chem. (Liebig), **216**, 311.

² *Ibid.*, **216**, 314.

³ Cf. V. Meyer: Ber. d. chem. Ges., **13**, 2344.

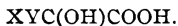
⁴ Bull. Soc. Chim., [3], **33-34**, 1, 49. Compt. rend., **139**, 740-742.

⁵ Ann. Chem. (Liebig), **335**, 247-279.

carbinols, which are not tautomeric compounds. Furthermore, the conversion of benzoyl or acetyl carbinol into *r*-mandelic or *r*-lactic aldehyde by dissociation and subsequent addition, as assumed by Zincke (see above) is excluded, as Nef has shown that an equimolecular mixture of formaldehyde and acetaldehyde gives absolutely no *r*-lactic acid in the presence of cupric hydroxide and sodium hydroxide. Nef, therefore, came to the conclusion that benzoyl- and acetylformaldehydes, respectively, must first be formed in the reaction under discussion and that the conversion of the resulting aldehydes into lactic and mandelic acids is due to a benzilic acid rearrangement. As is well known, almost all orthodicarbonyl compounds,

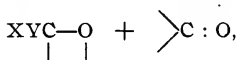


whether in open chains or closed cycles, undergo such a rearrangement or conversion, by absorption of 1 molecule of water, into α -hydroxy acids,



In some cases, as with hexaketomethylene and diketosuccinic acid, this rearrangement takes place quantitatively in dilute aqueous solution; in most instances it requires the presence of more or less concentrated aqueous caustic alkalies, or at times even solid potassium hydroxide at higher temperatures. Nef¹ has presented the following interpretation of this remarkable rearrangement: The orthodicarbonyl com-

pound $\begin{array}{c} \text{XC} : \text{O} \\ | \\ \text{YC} : \text{O} \end{array}$ dissociates into $\text{XYC} : \text{O}$ and $\begin{array}{c} \diagup \\ \text{C} : \text{O} \\ \diagdown \end{array}$; the products of dissociation, in their active molecular form



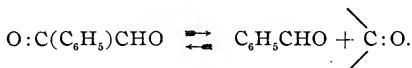
unite to form the addition product,

¹ Ann. Chem. (Liebig), **335**, 272-273.

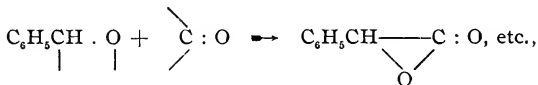
proves, in a most convincing manner, that this substance, in the process of transformation into *r*-mandelic acid by a benzilic acid rearrangement, must first be dissociated into benzaldehyde and carbonic oxide, as assumed by Nef. The facts are these: A. Benzoylformaldehyde gives, with freshly precipitated mercuric or silver oxides, alone or in the presence of caustic alkalis, benzoic and carbonic acids only; separate experiments with mandelic and benzoylformic acids and the oxides named prove that this oxidation cannot possibly have taken place with the intermediate formation of these acids. B. Benzoylformaldehyde, with cupric oxide and caustic alkalis, as well as with potassium ferricyanide and potassium hydroxide, gives, practically, *r*-mandelic acid *only*. C. Benzoylformaldehyde, with aqueous potassium permanganate, in the cold, gives, practically, only benzoic acid; under the same conditions, but in the presence of caustic alkalis, about equal amounts of benzoylformic, benzoic and carbonic acids are formed. It is, moreover, certain that the benzoylformic acid is formed from *r*-mandelic acid obtained by a benzilic acid rearrangement of the aldehyde, and not through a direct oxidation of the aldehyde, and its proportion undoubtedly varies with the concentration of the alkali used.

The only possible interpretation of the results, A, B and C, is the following:

I. Benzoylformaldehyde is partially dissociated into carbonic oxide and benzaldehyde,



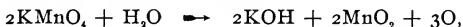
II. The relative rate of transformation of the products of dissociation I into *r*-mandelic acid,



and the relative rate of oxidation of these dissociation products into benzoic and carbonic acids varies in cases A, B and C, re-

spectively. In other words, benzaldehyde and carbonic oxide, reacting, as is known, very readily with the oxides of mercury and silver, are entirely oxidized in the presence of these reagents before they can unite to form *r*-mandelic acid (case A).

In the presence of alkalies and cupric hydroxide or potassium ferricyanide, on the other hand, since these are very mild oxidizing agents, *only* a benzilic acid rearrangement takes place, *i. e.*, the formation of *r*-mandelic acid (case B). If potassium permanganate, without alkalies, is used on benzoylformaldehyde no rearrangement to *r*-mandelic acid occurs, but with alkalies present (case C) about 50 per cent of oxidation of its dissociation products and 50 per cent of transformation to *r*-mandelic acid takes place. This is not surprising, since in oxidation by potassium permanganate,



the amount of alkali set free in the reaction is only sufficient to form salts with the benzoic and carbonic acids which are formed; no experiments were carried out to determine the velocity of the transformation of benzoylformaldehyde into *r*-mandelic acid with varying concentration of the alkali.

These results, therefore, establish experimentally the correctness of Nef's interpretation of the benzilic acid rearrangement; there are, furthermore, numerous observations in the literature which prove that many ortho or 1,2-dicarbonyl compounds undergo dissociation into carbonic oxide and a monocarbonyl derivative at comparatively low temperatures, and this must also be considered as evidence pointing to the same conclusion. Thus benzil and hydroxyoxalacetic ester readily decompose, at 250°–300°, into carbonic oxide, benzophenone and hydroxymalonic ester, respectively.

EXPERIMENTAL PART.

Preparation of Benzoyl Carbinol.—Owing to the extreme sensitiveness of benzoyl carbinol, especially towards alkaline reagents, the methods heretofore used in its preparation¹ were found to give very unsatisfactory yields; the same is true

¹ Graebe: Ber. d. chem. Ges., 4, 34. Hunnius: *Ibid.*, 10, 2910. O. Fischer and Busch: *Ibid.*, 24, 2689. Zincke: Ann. Chem. (Liebig), 216, 306.

when bromacetophenone or α -bromophenylacetaldehyde are digested with potassium formate and methyl alcohol, methods which give acetol quantitatively with the corresponding derivatives in the fatty series.¹

The hydrolysis of benzoyl carbinol acetate by means of 17 parts of boiling water, for 12 hours, was finally found to be the best means of preparing this substance; bromacetophenone was made from 75 grams of acetophenone, according to the directions of Möhlán² and the crude oil, 124 grams, precipitated by water, was converted into the acetate by digesting for 3 hours, under a reversed condenser, at 125°–130°, with 310 grams of glacial acetic acid and 100 grams of fused sodium acetate. One hundred grams of crude acetate were thus obtained by addition of water, extraction with ether and removal of the acetic acid by washing with sodium carbonate solution; on distillation under 10–15 mm., 5.3 grams of this boiled below 130° and the remainder, 89 grams, 80 per cent of the theoretical, at 145°–155°, leaving 5 grams of tar in the distilling flask. On hydrolysis of the main fraction of the acetate, as mentioned above, 49 grams of pure benzoyl carbinol, crystallized from ether-ligroin and melting at 85°–86°, were obtained, besides 3.5 grams of tar, insoluble in boiling water. Benzoyl carbinol boils, according to the observations of Nef, without the slightest decomposition, at 118°–120° (11 mm.); on distilling 10 grams of it, under 10 mm. pressure, through a combustion tube filled with pumice, kept at 400°–440°, in a 28 burner furnace, 7 grams of carbinol were recovered unchanged (time, 10–15 minutes); on repeating the experiment, but raising the temperature to 580°–600°, much decomposition with gas evolution took place. The liquid decomposition products, 2.50 grams, were proved to contain benzene and benzaldehyde, which was identified as phenylhydrazone; 0.80 gram, m. p. 158°, was obtained. A strong odor of formaldehyde was noticed in the apparatus. This proves that benzoyl carbinol dissociates, by heat, in a manner analogous to acetol,³ into benzaldehyde and formaldehyde,

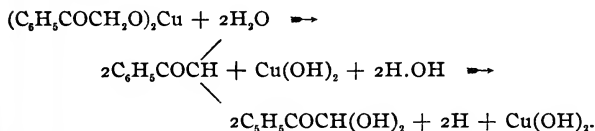
¹ Ann. Chem. (Liebig), 335, 260, 265.

² Ber. d. chem. Ges., 15, 2464.

³ Nef: Ann. Chem. (Liebig), 335, 250.



Action of Benzoyl Carbinol on Copper Salts.—In the cold the first stage in the action of aqueous copper acetate and copper sulphate, respectively, on benzoyl carbinol is the conversion into benzoylformaldehyde, as was proved by special experiments; in the former case cuprous oxide is formed and in the latter metallic copper is deposited. It is extremely probable that, in both cases, there is first an intermediate formation of cupric benzoyl carbinol,¹ and this, like all salts of primary and secondary alcohols, has a much lower dissociation point than the corresponding alcohol; consequently the following reaction takes place:



The atomic hydrogen thus formed then reduces the cupric salt present either to metallic copper or to the cuprous state.

Benzoyl Carbinol and Cupric Acetate.—Five grams of benzoyl carbinol, dissolved in 120 cc. of warm water, were added to a solution of 22 grams (3 mols.) of crystallized copper acetate, in 350 cc. of water; the temperature of the resulting solution was at first 35° and cuprous oxide began to separate out almost immediately. The mixture was allowed to attain room temperature and was then left standing for 14 days. The precipitate of cuprous oxide was found to weigh 3.5 grams and the aqueous filtrate was extracted 18 times with ether. The oily residue, obtained on evaporating the moist ether extracts, was freed from acetic and other acids by digestion with water and 4 grams of calcium carbonate; the aqueous filtrate, again extracted thoroughly with ether, yielded, on evaporation of the moist ether and on drying over sulphuric acid *in vacuo*, 3.9 grams of a neutral, crystalline, pungent smelling substance,

¹ Nef: Ann. Chem. (Liebig), 335, 275.

melting at 70° ; on crystallizing from water it melted at 78° and remained unchanged when mixed with an equal amount of v. Pechmann's¹ benzoylformaldehyde monohydrate. The identity of the product obtained with benzoylformaldehyde was furthermore established by the following tests:

a. One-half gram, dissolved in 40 cc. of water, was treated with 0.2 gram of powdered calcium hydroxide, in the cold; the solution turned yellow at once and after standing 12 hours gave, on acidifying with hydrochloric acid and thorough extraction with ether, 0.5 gram of *o*-mandelic acid, m. p. $118^{\circ}.5$.

b. One-half gram of the aldehyde, dissolved in 4 cc. of 50 per cent alcohol gave, on addition of 0.05 gram of potassium cyanide and subsequent addition of water, 0.3 gram of the yellow benzoin derivative of benzoylformaldehyde,



first obtained by Söderbaum;² the melting-point of this product was found to be 180° , with previous darkening at 176° , whereas Söderbaum found 170° .

c. The benzoylformaldehyde obtained on treatment with Fehling's solution does not give the slightest reduction to cuprous oxide. This is in harmony with v. Pechmann's observation; with silver oxide, on the other hand, a reduction to metallic silver takes place at higher temperatures (see below). Since pure benzoylformaldehyde and benzil are without action on Fehling's solution, it is very probable that other pure orthodicarbonyl compounds, such as glyoxal, acetylformaldehyde and diketosuccinic acid, must behave in a similar manner towards this reagent, as it must simply transform the compounds, by a benzilic acid rearrangement, into the corresponding α -hydroxy acids. I therefore conclude that acetylformaldehyde, which is the perfect analogue of benzoylformaldehyde in the fatty series, and which has recently been isolated by Harries and Turk,³ must have contained some impurity, as the product obtained by them is described as reducing Fehling's solution. Finally, it should be mentioned that, in addition to

¹ Ber. d. chem. Ges., **22**, 2557.

² *Ibid.*, **24**, 1381, 3038.

³ *Ibid.*, **38**, 1630.

the main neutral reaction product obtained in the experiment above described, the aqueous solutions containing lime salts of acids gave, when worked up by the method described below, 0.15 gram of benzoic acid, m. p. 121° , and 0.35 gram of mandelic acid, m. p. 118° , but no trace of benzoylformic acid.

Benzoyl Carbinol and Copper Sulphate.—No action was noticed on mixing cold, aqueous solutions of 5 grams of benzoyl carbinol and 18.2 grams (2 mols.) of crystallized copper sulphate, the total volume being 400 cc., but on allowing the mixture to stand outdoors in the sunlight, for 2.5 months, the solution had changed to dark green, the action being accompanied by a deposition of copper. It was now warmed for 6 hours at 50° – 60° , finally, for a short time, at 100° , and then filtered from the copper, 1.10 grams. The aqueous filtrate was extracted with ether and the reaction products separated into acid and neutral portions, as mentioned above, by powdered calcium carbonate. There were obtained, as reaction products, 2.7 grams of benzoylformaldehyde monohydrate, melting at 78° , containing traces of unchanged carbinol, and 0.5 gram of *r*-mandelic acid, melting at $118^{\circ}.5$, besides 0.25 gram of benzoic acid.

The quantitative separation and determination of the relative amounts of benzoic, benzoylformic and *r*-mandelic acids formed in the various cases was always carried out as follows: The acid mixture was first distilled with steam, which carried over only benzoic acid. The non-volatile portion was then treated with phenylhydrazine, dissolved in an equal volume of 50 per cent acetic acid and, after 24 hours' standing, benzoylformic acid phenylhydrazone separated out completely. It was purified by dissolving in dilute sodium carbonate solution, reprecipitating by dilute sulphuric acid and crystallizing from hot benzene.¹ From this the amount of keto-acid present could be determined by calculation. The aqueous filtrate from the phenylhydrazone, containing only *r*-mandelic acid, was worked up for this acid by thorough extraction with ether and subsequent washing with dilute sulphuric acid. The residue, after the evaporation of the ether, was heated at 100° (25–30 mm.)

¹ Cf. Nef: *Ann. Chem.* (Liebig), **280**, 295.

in order to remove the acetic acid. The *r*-mandelic acid was finally crystallized from a mixture of ether and ligroin (70°–80°).

The Behavior of Benzoylformaldehyde towards Copper Salts at 100°.—The most striking property of benzoylformaldehyde is its transformation into *r*-mandelic acid, which takes place very rapidly with all aqueous caustic alkalies, even in the cold and in most dilute solutions. This was first observed by v. Pechmann and Söderbaum¹ and has been repeatedly confirmed by me.

The conversion of the aldehyde into *r*-mandelic acid also takes place by heating with aqueous solutions of various copper salts, as is proved by what follows: Two grams of benzoylformaldehyde hydrate and 2.97 grams of crystallized copper acetate, dissolved in 70 cc. of water, were boiled for 1 hour. There was a gradual separation of insoluble greyish-white crystalline copper mandelate.² The precipitate was dissolved in dilute hydrochloric acid and, on extracting well with ether as described, 1.7 grams of pure *r*-mandelic acid, m. p. 118°.5, were obtained. A special experiment with a solution of 2 grams of benzoylformaldehyde and 8.10 grams of copper acetate, in 225 cc. of water, proved that, on standing 3 days at ordinary temperatures, no transformation into *r*-mandelic acid had taken place. On extracting the solution 18 times with ether and heating with calcium carbonate in the usual manner, 1.44 grams of aldehyde were recovered unchanged. A solution of 1 gram of benzoylformaldehyde hydrate and 1.25 grams of crystallized copper sulphate, in 100 cc. of water, was heated at 130°, for 7 hours; 0.55 gram of bluish-white copper mandelate precipitated, from which 0.30 gram of the pure acid was obtained. The aqueous filtrate yielded 0.5 gram of oily residue, which was proved to be mainly unchanged aldehyde by conversion into 0.40 gram of pure *r*-mandelic acid, by means of sodium hydroxide.

Special experiments with an aqueous solution of *r*-mandelic acid, containing molecular quantities of copper acetate or cop-

¹ *Loc. cit.*

² *Ann. Chem.* (Liebig), 18, 320.

per sulphate, proved that in both cases there is practically complete precipitation of copper mandelate on warming on a boiling water-bath, acetic and sulphuric acids, respectively, being thus set free.

Benzoyl Carbinol and Copper Salts at 100°.—In view of the results just presented, the following experiment with benzoyl carbinol and aqueous copper acetate needs no further elucidation. A solution of 5 grams of benzoyl carbinol and 22 grams of crystallized copper acetate (3 mols.) dissolved in 425 cc. of water, was heated, after standing 12 hours, first at 50°–60° and finally for 3 hours at 100°. The precipitate, which at first consisted only of cuprous oxide, gradually became covered with cupric mandelate. The total weight was 10 grams and from this, by treatment with dilute hydrochloric acid and extraction with ether, 4 grams of pure mandelic acid were obtained. The aqueous filtrate, acidified with dilute sulphuric acid and extracted with ether, etc., gave 0.10 gram of benzoic acid, melting at 121°, 0.20 gram of *r*-mandelic acid, melting at 118°.5, and a trace of benzoylformic acid.

Benzoyl Carbinol and Cupric and Sodium Hydroxides.—Benzoyl carbinol and acetol, respectively, reduce Fehling's solution very rapidly in the cold. The quantity of oxygen used in the oxidation of the acetol has been determined by W. H. Perkin, Jr.,¹ and others, and found to be 1 atom. It is practically certain, from Zincke's experiments with acetol and benzoyl carbinol,² and from the following one with benzoyl carbinol that *r*-lactic and *r*-mandelic acids, respectively, are formed in this oxidation process. Furthermore, the oxidation proceeds through an intermediate formation of acyl-formaldehyde, which then, in the presence of the strong caustic alkali, immediately undergoes a benzilic acid rearrangement.

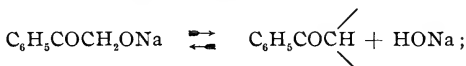
The benzoyl carbinol undoubtedly forms a sodium or potassium salt with the caustic alkali present,³ which, having a low

¹ J. Chem. Soc., 59, 788.

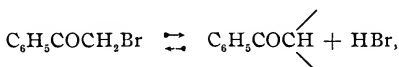
² Loc. cit. Cf. Nef: Ann. Chem. (Liebig), 335, 273.

³ Nef: Loc. cit.

dissociation point, is relatively much dissociated at ordinary temperatures into benzoyl methylene,



the latter then takes up the hydroxyl ions present, giving benzoylformaldehyde hydrate and the atomic hydrogen or kation thus set free reduces the bivalent copper to cuprous oxide. Since bromacetophenone is also partially dissociated into benzoyl methylene and hydrogen bromide,



at ordinary temperatures, it is to be expected that this substance must give, with Fehling's solution as well as with sodium and cupric hydroxides, exactly the same results as benzoyl carbinol; this is proved by what follows: Five grams of benzoyl carbinol, in 310 cc. of water, were added to a solution of 18.10 grams (2 mols.) of crystallized copper sulphate, in 90 cc. of water. On the addition of 8 grams of sodium hydroxide (5 mols.), dissolved in 24 cc. of water, reduction to cuprous oxide took place at once, in the cold. The mixture was finally warmed for 15 minutes on a water-bath, filtered and the yellow filtrate evaporated to dryness under 15–20 mm. pressure (bath 100°). On acidifying with hydrochloric acid and extracting 7 times with ether, a total of 5.15 grams of reaction product was obtained. This gave, by working up in the usual manner, 3.70 grams of *r*-mandelic acid, melting at 118°; 0.10 gram of pure benzoic acid and 0.25 gram of benzoylformic acid (from 0.40 gram of the hydrazone).

Bromacetophenone and Cupric and Sodium Hydroxides.—Five grams of bromacetophenone, suspended in a solution of 12.5 grams (2 mols.) of crystallized copper sulphate, in 300 cc. of water, were treated with 10 grams of sodium hydroxide (5 mols.) in 100 cc. of water. On shaking violently, reduction to cuprous oxide took place at once and, after standing in the cold for 24 hours and then working up as in the previous case,

I obtained 2.30 grams of pure mandelic acid, besides 1 gram of unchanged bromacetophenone. When this experiment was repeated at 100°, for 8 hours, only 2.40 grams of crude reaction products were extracted by ether, and from this I obtained 0.50 gram of benzoic acid, 0.41 gram of mandelic acid and 0.25 gram of benzoylformic acid.

Benzoyl Carbinol, Potassium Hydroxide and Potassium Ferricyanide.—Five grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to a mixture of 60.4 grams of potassium ferricyanide and 10.4 grams of potassium hydroxide, in 400 cc. of water, the resulting temperature being 38°. After standing 12 hours, the mixture was worked up by acidifying with dilute sulphuric acid and extracting 6 times with ether. Three and seven-tenths grams of pure mandelic acid, besides 0.30 gram of benzoic acid, were finally obtained. A special experiment with 0.5 gram of benzoylformaldehyde hydrate, dissolved in 25 cc. of water and 18 cc. of a solution containing 3.25 grams of potassium ferricyanide and 0.85 gram of potassium hydroxide, after standing 4 hours in the cold, gave 0.40 gram = 80 per cent of the theoretical amount of pure mandelic acid. It is obvious, therefore, without further comment, that the reactions with benzoyl carbinol and alkaline copper and ferricyanide solutions proceed in a perfectly analogous manner. Finally, a special experiment with 2 grams of mandelic acid, 10.80 grams of potassium ferricyanide, 3 grams of potassium hydroxide, dissolved in 150 cc. of water, proved that, after 24 hours' standing in the cold, no oxidation of the acid had taken place, as 1.80 grams were recovered unchanged by working up in the usual manner.

Acetophenone, Potassium Ferricyanide and Potassium Hydroxide.—According to the literature,¹ acetophenone gives benzoylformic and benzoic acids, by oxidation with the reagents just named. These observations were confirmed and it was proved with special care that no trace of *r*-mandelic acid is formed in this case. This shows that the oxidation reactions with acetophenone cannot possibly proceed in a manner analogous to those of benzoyl carbinol and bromacetophenone; there was,

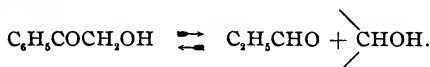
¹ Buchka and Irish: Ber. d. chem. Ges., 20, 389.

a priori, a possibility of this. Five grams of acetophenone were added to a solution containing 68 grams of potassium ferricyanide (2.5 atoms of oxygen), 16 grams of potassium hydroxide and 800 cc. of water. The reaction sets in at once, in the cold; after 36 hours' standing and filtering from a small amount of yellow, flocculent precipitate, the solution was acidified with dilute sulphuric acid and worked up for acids by extracting with ether, etc. I obtained 1.05 grams of benzoylformic acid, 0.20 gram of benzoic acid, 0.70 gram of tar, but no mandelic acid.

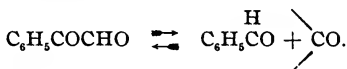
Benzoyl Carbinol and Potassium Permanganate.—A solution of 5 grams of benzoyl carbinol, in 120 cc. of warm water, was slowly added to 7.40 grams of potassium permanganate (3 mols.) dissolved in 300 cc. of water, which was cooled by running water. After 3 hours' standing the excess of permanganate was removed by the addition of alcohol and the colorless filtrate worked as usual for acids. Three and nine-tenths grams of pure benzoic acid, containing no trace of mandelic or benzoylformic acids, were obtained. As mentioned in the introduction, the results are quite different if the oxidation is carried on in the presence of caustic alkalies. Five grams of benzoyl carbinol, in 220 cc. of water, were added, in the cold, to a solution containing 11.60 grams of potassium permanganate (2 mols.) and 2.94 grams of sodium hydroxide (2 mols.), in 200 cc. of water. After 12 hours' standing the aqueous filtrate, when acidified with dilute sulphuric acid and extracted with ether, gave 5.3 grams of crude acid material. This was resolved into 2.3 grams of benzoylformic acid and 1.7 grams of benzoic acid.

Benzoylformaldehyde and Potassium Permanganate.—Two grams of benzoylformaldehyde, in 44 cc. of water, and a solution of 4.16 grams of potassium permanganate (2 mols.) in 75 cc. of water, gave, after standing 3 hours in the cold, 1.5 grams of pure benzoic acid. In an experiment using the same amounts of material as in the one just presented, but having, in addition, 1.04 grams of sodium hydroxide (2 mols.) present, 0.87 gram of benzoylformic acid and 1.2 grams of benzoic acid

were obtained. It is obvious that the benzoic acid formed in the experiment with permanganate alone may come, in the case of benzoyl carbinol, in part from an oxidation of the dissociated portions,



In the presence of caustic alkali, however, as well as in all cases with benzoylformaldehyde, this must be formed *exclusively* from the oxidation of the dissociated benzoylformaldehyde hydrate molecules,



Regarding the formation of benzoylformic acid in the experiments, it is certain that this results from an intermediate transformation of the benzoylformaldehyde by the caustic alkali present into *r*-mandelic acid, which, as will be shown directly, must oxidize at once under the conditions of the experiment to benzoylformic acid.

The formation of benzoylformic acid cannot possibly be ascribed to a *direct* oxidation of the molecular benzoylformaldehyde,

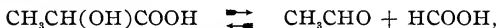


because, in that case, this acid should have been obtained from the aldehyde by aqueous permanganate alone and without the formation of any benzoic acid. Special experiments by Buchka and Irish¹ with potassium benzoylformate and an excess of permanganate prove that this acid is absolutely unchanged even after 14 days' standing, and this fact was confirmed. The benzoic acid, which is formed exclusively from benzoyl carbinol, as well as from benzoylformaldehyde with aqueous permanganate must, therefore, come from a burning of these molecules in the dissociated condition. When caustic alkali is present this is still one of the main results, but in that case

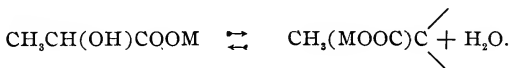
¹ Ber. d. chem. Ges., 20, 387. Cf. Beilstein: *Ibid.*, 17, 840.

there is about an equal amount of transformation of the benzoylformaldehyde into *r*-mandelic acid, which is then at once further oxidized.

The experiments of Nef¹ have shown very decisively that the free *r*-lactic acid is dissociated relatively *more* into acetaldehyde and formic acid,



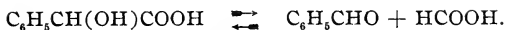
whereas the salts of this acid, especially in the presence of caustic alkalies, which prevent hydrolysis and admit of further salt formation, are relatively *more* dissociated into water and ethylenecarboxylic acid,



This explains why lactic acid in the free condition, or by the hydrolysis of its salts, *invariably* gives only acetic, formic and carbonic acids on treatment with oxidizing agents, and why the lactates, on the other hand, by the oxidation of the secondary alcohol group, *invariably* give acetylformic acid only. My own experiments with the analogous *r*-mandelic acid have confirmed in every way these conclusions of Nef and show that they apply, word for word, in this case also. Beilstein has shown² that *r*-lactic acid with alkaline permanganate solutions in the cold, gives a large yield of pyruvic acid. I have found that *r*-mandelic acid, under similar conditions, even when a great excess of alkaline potassium permanganate is added, gives benzoylformic acid quantitatively. This is, in fact, by far the best method for preparing benzoylformic acid. It is important to realize that an excess of alkali should be present, in which case no trace of benzoic acid can be formed. If free mandelic acid, or even a mandelate, be treated, in aqueous solution, with potassium permanganate, there is a chance for formation of some benzoic acid, because free mandelic acid, formed by hydrolysis, must be present and this gives, by oxidation, benzoic and carbonic acids only, because it is dissociated mainly according to the scheme

¹ Ann. Chem. (Liebig), **335**, 296.

² Loc. cit.



Benzoyl Carbinol and Silver Oxide.—Three grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to 2.25 mols. of freshly precipitated and well washed silver oxide, from 16.8 grams of silver nitrate; no action takes place until the temperature is raised to 70°. After heating 4 hours on a boiling water-bath, during which time a steady stream of carbon dioxide was evolved, the reduction to silver was complete. One and nine-tenths grams of benzoic acid, 0.30 gram of unchanged carbinol and 10 grams of silver were the only reaction products. In a second experiment, using 4 grams of carbinol, silver oxide from 20 grams of silver nitrate (4 mols.), 4.7 grams of sodium hydroxide (4 mols) and water (total volume 350 cc.), reduction took place rapidly at the ordinary temperature. Pure benzoic acid, 3.32 grams = 92 per cent of the theoretical amount, and 12.60 grams of silver were the only products found.

Benzoylformaldehyde and Silver Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated and well washed silver oxide, from 2.52 grams of silver nitrate. No action took place on standing over night. Therefore the mixture was heated for 3 hours, at 70°–100°, when a copious evolution of carbon dioxide was observed. There were obtained 0.75 gram of pure benzoic acid, 92 per cent of the theory, silver and carbon dioxide, as the only reaction products. On repeating the experiment, having, in addition, 1.32 grams of sodium hydroxide (2 mols.) present, a reduction of silver took place at once, in the cold. Eight-tenths of a gram of pure benzoic acid, 1.77 grams of silver and only a few milligrams of *r*-mandelic acid were obtained.

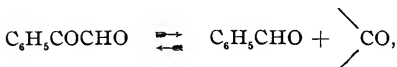
Mandelic Acid and Silver Oxide.—In a special experiment with 1 gram of mandelic acid, 1 mol. of freshly precipitated silver oxide, 0.53 gram = 2 mols. of sodium hydroxide and 50 cc. of water, it was found that no trace of reduction to silver took place on heating for 6 hours on a boiling water-bath; the acid was, furthermore, recovered entirely unchanged. Two and

eight tenths grams of pure silver mandelate,¹ dissolved in 350 cc. of water and treated on a boiling water-bath for 4 hours, with 2 mols. of freshly precipitated and well washed silver oxide, from 8.10 grams of silver nitrate, gave, on working up in the usual manner, 0.40 gram of benzoic acid, besides 0.55 gram of unchanged *r*-mandelic acid, but no trace of benzoylformic acid. These results are in harmony with the work of Nef² on lactic acid. The observations prove, therefore, with great precision, that no mandelic acid can have been formed as an intermediate product in the action of silver oxide alone, or in the presence of sodium hydroxide, on benzoyl carbinol or benzoylformaldehyde, respectively.

Benzoylformic Acid and Silver Oxide.—Silver oxide, in the presence of sodium hydroxide, is without effect on benzoylformic acid in the cold. On heating to 100°, however, reduction to silver and a quantitative transformation to carbonic and benzoic acids takes place. Thus a mixture of 0.50 gram of benzoylformic acid, 0.52 gram of sodium hydroxide, 1 mol. of silver oxide and 25 cc. of water gave, on heating during 3 hours, at 100°, 0.40 gram of benzoic acid.

One and two-tenths grams of silver benzoylformate, dissolved in 300 cc. of water containing 1.25 mols. of well washed silver oxide, remained unchanged after 3 hours' heating at 30°, but, on heating at 100°, carbon dioxide began to be evolved and, after 3 hours' heating, 0.50 gram of pure benzoic acid was obtained as a reaction product.

These experiments prove that benzoylformic acid cannot have been formed as an intermediate product in the action of silver oxide alone, or in the presence of caustic alkalies, on benzoyl carbinol or benzoylformaldehyde; it is certain, therefore, that the benzoic and carbonic acids obtained in these cases result from a direct oxidation of the dissociation products of benzoylformaldehyde,



¹ Winckler : *Ann. Chem. (Liebig)*, **18**, 310.

² *Ibid.*, **335**, 277, 297, 315.

which, in these instances, cannot recombine to form *r*-mandelic acid because their speed of oxidation must be far more rapid than the velocity of the benzilic acid rearrangement.

The corresponding experiments, using freshly precipitated mercuric oxide in place of silver oxide, lead to exactly the same conclusions; they are, therefore, simply mentioned here without further comment.

Benzoyl Carbinol and Mercuric Oxide.—Five grams of benzoyl carbinol, dissolved in 350 cc. of water, were treated with an emulsion of freshly precipitated mercuric oxide, from 22 grams of mercuric chloride, in 200 cc. of water. No action took place in the cold, but on heating for 9 hours on a water-bath, much carbon dioxide was evolved. Pure benzoic acid, 3.75 grams = 83 per cent of the theoretical, besides 0.35 gram of unchanged carbinol were obtained as reaction products. In a second experiment, using the same amounts of material, but adding also a solution of 6 grams of sodium hydroxide in 50 cc. of water, reduction to mercury took place at once, in the cold; after 12 hours' standing, 4.10 grams of pure benzoic acid = 91.3 per cent of the theory, were obtained.

Benzoylformaldehyde and Mercuric Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated mercuric oxide and thereupon a solution of 0.52 gram of sodium hydroxide (2 mols.) in 25 cc. of water were added. Reduction took place at once, in the cold and, after 12 hours' standing, 0.85 gram (theory 0.88 gram) of pure benzoic acid was obtained, but no trace of mandelic acid.

A special experiment with 2 grams of mandelic acid, 1 mol. of precipitated mercuric oxide and 1.60 grams of sodium hydroxide, in 50 cc. of water, proved that no reduction to mercury took place, even on heating 2.5 hours on a water-bath; 1.90 grams of mandelic acid were subsequently recovered unchanged. Finally, it should be emphasized, that my results with mercuric oxide and benzoyl carbinol are in accord with the corresponding ones obtained by Nef with acetol.¹ Kling²

¹ Ann. Chem. (Liebig), **335**, 276.

² Bull. Soc. Chim., [3], **33**, 1, **34**, 49.

states that acetol is converted by mercuric hydroxide *quantitatively* into lactic acid ; this is obviously a mistake.

On the Behavior of Benzoyl Carbinol, Benzoylformaldehyde, Mandelic Acid and Benzoylformic Acid towards Chromic and Dilute Sulphuric Acids.—The following quantitative experiments, which show that these substances give benzoic and carbonic acids only, on oxidation in the cold with chromic acid in dilute sulphuric acid solution, are simply recorded here ; they require no further elucidation :

a. A mixture of 5 grams of benzoyl carbinol, 8.10 grams of potassium dichromate (2.25 atoms of oxygen), 10.8 grams of sulphuric acid and 400 grams of water gave, after standing 2 days in the cold, 2.10 grams of benzoic acid and 1.70 grams of unchanged carbinol.

b. One-half gram of benzoylformaldehyde hydrate, 0.74 gram of potassium dichromate, 0.97 gram of sulphuric acid and 70 cc. of water gave, after 2 days' standing in the cold, 0.44 gram of pure benzoic acid.

c. One gram of mandelic acid, 1.46 grams of potassium dichromate, 5.76 grams of sulphuric acid and 70 cc. of water gave, on standing 24 hours in the cold, 0.75 gram of benzoic acid.

d. One-half gram of benzoylformic acid, 0.41 gram of potassium dichromate, 0.60 gram of sulphuric acid and 50 cc. of water gave, on standing over night in the cold, 0.40 gram of benzoic acid.

PART II.

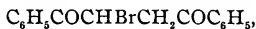
ON THE BEHAVIOR OF BENZOYL CARBINOL TOWARDS ALKALIES ; A REVISION OF PAAL AND SCHULZE'S WORK ON THE α - AND β -HALOGEN DIPHENACYLS.

On treatment of acetol, with caustic alkalies, under the most varied conditions, Nef never obtained a trace of *r*-lactic acid but mainly neutral, deep red colored resins which were considered by him to be polymerized acetylmethylene resin.¹ Benzoyl carbinol behaves in an entirely similar manner towards caustic alkalies, as well as towards alcoholic potassium hy-

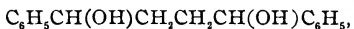
¹ Ann. Chem. (Liebig), 335, 278.

droxide and sodium ethylate. A small quantity of benzoic acid, entirely free from traces of *r*-mandelic acid, is invariably formed; the main reaction products, however, consist of dark yellow, non-volatile resins, in which no trace of *cis*- or *trans*-dibenzoylethylene,¹ but at times traces of *trans*-tribenzoylcyclotrimethylene, melting at 295°, ² were found. The resins obtained could, moreover, never be converted into solids or into crystalline derivatives.

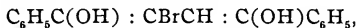
Since the monohalogenated acetophenones give, on treatment with various reagents, such as sodium acetoacetic ether, ammonia and, especially, with alcoholic potassium hydroxide or sodium ethylate (one-half mol.) large quantities of so-called space isomeric α - and β -halogen diphenacyls,³ it was thought possible that oxyacetophenone might, on similar treatment, first give the corresponding space isomeric α - and β -oxydiphenacyls; consequently, attempts were made to obtain these products first by synthesis directly from the so-called α - and β -bromdiphenacyls. Paal and Schulze have made an especially exhaustive study of these two compounds.⁴ They find that they are totally different from the *real* γ -bromdiphenacyl,



obtained from *cis*- and *trans*-dibenzoylethylene and hydrogen bromide. In view of the fact that their products give, by reduction, small amounts of diphenacyl or its corresponding glycol,



and because a fourth isomeric, so-called δ -halogen diphenacyl was isolated, Paal and Schulze give to their α - and β -compound the following dienol formula,



which is, obviously, capable of giving four different space isomers.

¹ Ber. d. chem. Ges., **33**, 3784; **35**, 168.

² Paal and Schulze: *Ibid.*, **36**, 2425.

³ Fritz: *Ibid.*, **28**, 3028. Paal and his students: *Ibid.*, **19**, 3146; **22**, 3225; **28**, 2102; **29**, 2092; **32**, 530; **36**, 2405.

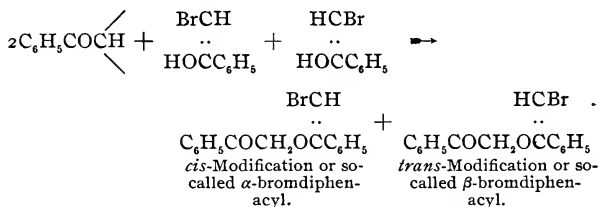
⁴ Ber. d. chem. Ges., **36**, 2386, 2405, 2415, 2425.

Further consideration shows, however, a great many serious objections to the formulae proposed by Paal and Schulze for their α -, β - and δ -compounds. It is noteworthy, (1) that they were never able to prove the presence of hydroxyl groups in their substances; (2) the compounds do not go over into furan derivatives by loss of water; (3) the α - and β -compounds have never been converted into the real γ -bromdiphenacyl, or *vice versa*, nor into one of the space isomeric dibenzoylthylenes.

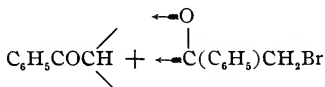
On the other hand, the real γ -halogen diphenacyls go over quantitatively, even on standing, and especially on heating with sodium acetate and acetic acid, into *trans*-dibenzoyl-ethylene.

In the present state of our knowledge there are, moreover, two other possible interpretations¹ of the reaction between bromacetophenone and sodium ethylate.

I. The benzoylmethylene, resulting from the dissociation of bromacetophenone, may react by alkylation with unchanged bromacetophenone *in the enol form*, and thus give rise to two space isomeric *cis*- and *trans*- α -phenacyloxy- ω -bromstyrols:

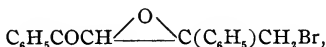


II. The benzoylmethylene might react with the active keto-bromacetophenone molecules present,

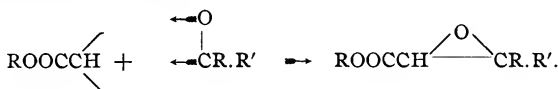


giving, by addition,² a glycid derivative,

¹ Cf. Nef: Ann. Chem. (Liebig), 310, 316; 335, 252, 261.
Cf. Nef: *Ibid.*, 335, 274. Foot-note.



which can exist in two space isomeric modifications. Professor Nef informs me that he believes the recent work of Claisen¹ and Darzens² on the conversion of ketones and some aldehydes into glycid derivatives by means of chloracetic ether, in the presence of sodium ethylate or sodamide, can only be rationally interpreted on this basis,³ *i. e.*, the methylenecarboxylate, present as a product of dissociation of chloracetic ether, simply unites with the various active ketone or aldehyde molecules present thus:



Interpretation II. cannot, however, possibly apply to the α - and β -halogendiphenacyl derivatives under consideration, because there is absolutely nothing known in their behavior justifying the presence of a glycid group. Consequently, we are forced to turn back to interpretation I. On looking over the work of Paal and Schulze on α - and β -bromdiphenacyl, it is noteworthy that one finds there a great deal of evidence in favor of the new formulae given under I. for these compounds—as, for instance, the absence of hydroxyl groups, the impossibility of converting these compounds into the real γ -bromdiphenacyl and *vice versa*, or into dibenzoylethylene or furfuran derivatives.

The most striking observation, repeatedly made, is the fact that α - and β -bromdiphenacyl, on treatment with dry halogen hydrides, in acetic acid solution, at the ordinary temperature, give a strong odor of bromacetophenone! If the so-called α - and β -bromdiphenacyls have the constitution assigned to them

¹ Ber. d. chem. Ges., 38, 693.

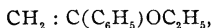
² Centrabl., 1905, I, p. 346.

³ A similar interpretation obviously applies to the formation of the product



obtained recently by Torrey from *p*-nitrosodimethylaniline and ethyl bromide. THIS JOURNAL, 34, 475 (1905).

above under I. they, or their addition products, must be resolved, quantitatively, in the cold, by dry hydrogen bromide, either into equal molecules of bromacetophenone and ω -dibromophenylmethylcarbinol, $C_6H_5CH(OH)CHBr_2$, or into 2 mols. of bromacetophenone. I propose, therefore, to carry out experiments in this direction at once. I have found, moreover, that α - and β -bromdiphenacyls give, on treatment with fused sodium acetate in acetic acid solution, at 100° , 66–68 per cent of the theoretical amounts, *viz.*, 2 mols. of benzoyl carbinol acetate (see below). The isomeric α - and β -acetoxydiphenacyls, as well as the β -oxydiphenacyl, also give a large yield of benzoyl carbinol acetate on similar treatment. These results are self-evident on the basis of the new formulæ for the compounds, but cannot be understood on the basis of those of Paal and Schulze. It should be remembered that the real, so-called γ -bromdiphenacyl gives, quantitatively, on treatment with sodium acetate and acetic acid, *trans*-dibenzoyl ethylene. The only observation which points in any way towards the old formulæ is the conversion of α - and β -bromdiphenacyl, by reduction with zinc dust and alcohol, into diphenacyl. This experiment was, therefore, repeated with the following result: Only a very small amount, about 10 per cent, of diphenacyl and about an equal quantity of acetophenone are formed. The main reaction product is a non-volatile oil—probably α -phenacyloxy-styrol, $CH_2 : C(C_6H_5)OCH_2COC_6H_5$, which at present is being further investigated. The formation of small quantities of diphenacyl in the above experiment is not difficult to understand on the basis of the new formulæ; one has only to remember that Claisen's analogous O-ethylacetophenone,¹



undergoes rearrangement by heat (for the explanation, *vide* Nef²) into C-ethylacetophenone, $C_6H_5COCH_2C_2H_5$. Furthermore, I have found that a mixture containing acetophenone and bromacetophenone, when heated in a sealed tube at 100° , with 10 per cent aqueous sodium hydroxide gives, among other

¹ Ber. d. chem. Ges., 29, 2931.

² Ann. Chem. (Liebig), 298, 372; 310, 316.

products, a very fair yield of diphenacyl—i. e., an alkylation of acetophenone by benzoylmethylene¹ takes place. It is, therefore, exceedingly probable that the small amount of diphenacyl obtained by Paal and Fritz in their experiments was formed in some such manner.

Finally, I consider the existence of the fourth so-called δ -ioddiphenacyl of Paal and Schulze as extremely doubtful; I think that it consists simply of the pure β -isomer; as has been shown by Paal and Schulze, it certainly gives exactly the same reactions and derivatives as the so-called β -compound and possesses, practically, the same crystalline form.²

Although, in view of what has just been presented, I consider the formulae of Paal and Schulze as practically untenable, I still use, in the following experimental part, their nomenclature for the α - and β -substituted diphenacyl derivatives. It is my intention to continue the study of these derivatives and to include also a study of the corresponding compounds in the aliphatic series.

The Conversion of α - and β -Bromdiphenacyl into Two Molecules of Benzoyl Carbinol Acetate.—On treating bromacetophenone with 0.5 mol. of alcoholic sodium ethylate and allowing the mixture to stand at 0° for 2 days, I obtained about equal quantities of α - and β -bromdiphenacyl;³ these were separated according to the directions of Paal, by means of cold benzene.

A solution of 1.55 grams (2 mols.) of fused sodium acetate, in 12 grams of glacial acetic acid, was cooled to 30°, 3 grams of β -bromdiphenacyl were added and the mixture heated for 6 hours, under a reversed condenser, in an oil-bath which was kept at 120°–130°. On pouring the dark red mixture into water, extracting with ether and washing with sodium carbonate solution, 3.10 grams of a dark brown oil were obtained. On distillation this gave 2.30 grams of pure benzoyl carbinol acetate, melting at 49°–50° and boiling at 160°–163° (18–20 mm.); this corresponds to 68 per cent of the theoretical amount. The

¹ Cf. Nef: *Ann. Chem. (Liebig)*, **310**, 316.

² *Ber. d. chem. Ges.*, **36**, 2411–2413.

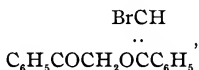
³ Cf. Fritz: *Ibid.*, **28**, 3028. Also Paal and Demeler: *Ibid.*, **29**, 2092.

product was further identified by its conversion by boiling water (*vide* Part I.) into benzoyl carbinol, melting at 86°.

A similar experiment with 3 grams of α -bromdiphenacyl, under practically the same conditions as in that just described, gave 0.50 gram of a reddish, non-volatile tar and 2.20 grams of pure benzoyl carbinol acetate, or 65.3 per cent of the theory.

The Conversion of α - and β -Acetoxydiphenacyl into Benzoyl Carbinol Acetate.—Paal and Schulze obtained β -acetoxydiphenacyl, melting at 98°, from the β -brom- or iodo-, as well as from the δ -ioddiphenacyl, on boiling with silver acetate and glacial acetic acid;¹ this compound can be best obtained, as I have found, by heating a mixture of 4 grams of β -bromdiphenacyl, 3.82 grams of potassium acetate and 40 cc. of absolute alcohol, for 3 hours, in a sealed tube, at 100°. An odor of acetic ether was noticed on opening the tube, and, on adding water, extracting with ether and crystallizing from ether-ligroin, 2.65 grams of pure product, 71 per cent of the theory, were obtained. Two grams of this were heated in a bath, at 120°–130°, for 5 hours, with a solution of 1.04 grams of fused sodium acetate and 5 grams of glacial acetic acid. On working up as in the previous cases, 0.88 gram of non-volatile tar and 0.90 gram of pure benzoyl carbinol acetate, boiling at 153° (12 mm.) and melting at 49°–50°, were obtained; this is 37 per cent of the theoretical amount.

According to Paal and Schulze, the α -bromdiphenacyl does not give the corresponding α -acetoxydiphenacyl on boiling with silver acetate and acetic acid; two isomeric, high-melting compounds, $(C_8H_6O_4)_4$, which they call bisanhydrooxydiphenacyl, or tetrabenzoyltetramethylene, were obtained.² Such a compound, $(C_8H_6O_4)_4$, could, naturally, also be formed from the *cis*- ω -brom- α -phenacyloxystyrol,



by simple loss of hydrogen bromide, and this is the main reason for assigning the *cis*-formula to the α -bromdiphenacyl, as

¹ Ber. d. chem. Ges., 36, 2416.

² *Ibid.*, 36, 2416.

above. I have, however, succeeded in obtaining totally different results by the action of alcoholic potassium acetate, 3.38 grams, on 3.75 grams of α -bromdiphenacyl, in a sealed tube, at 100° . Three and three-tenths grams of a thick, yellow oil were obtained, which I believe to be the crude α -acetoxydiphenacyl; it could not be obtained in a solid condition, but 2 grams of it, heated with sodium acetate and acetic acid, under exactly the same conditions as the β -acetate just described, gave 0.75 gram of non-distillable tar and 0.95 gram of pure distilled benzoyl carbinol acetate; this corresponds to 39.6 per cent of the theory.

β -Oxydiphenacyl.—On saponification of the β -acetoxydiphenacyl with alcoholic potassium hydroxide, Paal and Schulze obtained a yellow oil which, by treatment with sodium acetate and acetic anhydride, was converted back again into the original acetate; it must, therefore, have contained oxydiphenacyl. I have succeeded in obtaining β -oxydiphenacyl in the crystalline form; it is formed, besides an oily substance, not only from β -bromdiphenacyl, but also, probably by rearrangement into the β -space isomer, in smaller amounts (22 per cent yield) from α -bromdiphenacyl, by heating 2 grams of these compounds in 20 cc. of a methyl alcoholic solution of 1.5 mols. of potassium formate,¹ in sealed tubes, for 6 hours, at 100° . In the case of the β -isomer 0.95 gram of pure β -oxydiphenacyl was obtained, or 59 per cent of the theory; as the substance is very difficultly soluble in cold benzene and ether, it could readily be freed from a small amount, 0.65 gram, of the oily product. Crystallization from hot benzene gave microscopic needles of β -oxydiphenacyl, melting at 175° – 178° . In the α -series 0.35 gram of the β -oxy compound and 1.25 grams of yellow oil were obtained. Analysis of the crystalline product:

0.1874 gram substance gave 0.5204 gram CO_2 and 0.0984 gram H_2O .

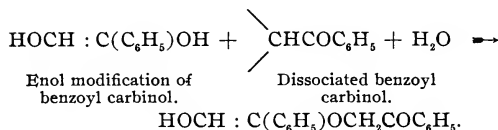
	Calculated for $\text{C}_{16}\text{H}_{14}\text{O}_3$	Found.
C	75.59	75.72
H	5.51	5.83

¹ Nef: Ann. Chem. (Liebig), 335, 260, 265.

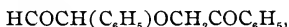
A mixture of 1 gram of β -oxydiphenacyl, 0.64 gram of fused sodium acetate and 7.10 grams of glacial acetic acid, heated in an oil-bath, at 130° , for 6 hours, gave 0.40 gram of pure distilled benzoylcarbinol acetate and 0.30 gram of non-volatile tar. It should be emphasized, in this connection, that benzoyl carbinol itself, on heating under the same conditions with sodium acetate and acetic acid, remains entirely unchanged.

One and one-half grams of β -oxydiphenacyl, heated for 6 hours, at 130° , with 6 grams of acetic anhydride, gave 0.6 gram of β -acetoxydiphenacyl, melting at 98° - $98^\circ.5$.

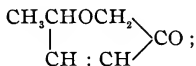
The question now arises whether any β -oxydiphenacyl is formed by the action of caustic alkalies on oxyacetophenone according to the equation,



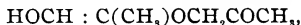
I can simply state here that none was found; it is, however, exceedingly probable that a compound of this constitution must, under the conditions employed, take up water to form the isomeric aldehyde,



and this, by loss of water, can easily go over into a condensation product. Interpreted on this basis, the condensation product, $\text{C}_6\text{H}_8\text{O}_2$, obtained by Peratoner and Leonardi,¹ from acetol and aqueous barium hydroxide, must possess the constitution,

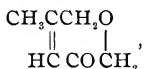


i. e., it must be 1-methyl-4-keto- Δ^2 -dehydrohexone, being formed from β -acetonyl- α,β -dihydroxypropylene,



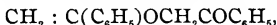
¹ Gazz. chim. ital., 30, 1, 577.

or the corresponding aldehyde, by loss of water. This corresponds, in general, very closely to the formula,



2-methyl-4-keto- Δ^2 -dehydrohexone, assigned to it by Peratoner and Leonardi, and explains all the known reactions of the compound equally well. In view of this, I am encouraged to study still further the yellow tars obtained by the action of caustic alkalis on acetol and benzoyl carbinol, respectively.

On the Reduction of β -Bromdiphenacyl by Zinc Dust and Alcohol.—On treatment of β -bromdiphenacyl with these reagents, V. Fritz¹ obtained small quantities of diphenacyl and acetophenone; this observation was confirmed by Paal and Demeler,² who state that, in addition, a large amount of non-volatile oil is formed. I have repeated this experiment with 8 grams of material, 40 grams of zinc dust and 100 cc. of ethyl alcohol, heating 2.5 hours on a boiling water-bath. Five and one-tenth grams of crude reaction product were obtained on filtering, adding water and extracting with ether. The acetophenone was removed by heating in a bath up to 160° (18 mm.); only 0.5 gram was thus obtained and identified by conversion into the phenylhydrazone.³ Three-tenths gram of diphenacyl, melting at 140°–142°, and converted into the characteristic di-oxime,⁴ melting at 202, were obtained from the oil left on adding a small amount of alcohol and stirring. The remainder, 4.30 grams, and, therefore, the main reaction product, consisted of a thick, non-volatile oil, whose study is to be continued. It is, in all probability, α -phenacyloxystyrol,



isomeric with diphenacyl and, therefore, formed by a direct reduction of β -bromdiphenacyl.

¹ Ber. d. chem. Ges., 28, 3033.

² *Ibid.*, 29, 2095.

³ Bischler: *Ibid.*, 16, 662.

⁴ Paal and Kapf: *Ibid.*, 21, 3057.

In conclusion, I wish to acknowledge my deep sense of gratitude to Professor Nef for his inspiring and careful guidance of this work.

THE GERMICIDAL ACTION OF POTASSIUM PERMANGANATE.

BY JAMES B. GARNER AND WALTER E. KING.

INTRODUCTORY PAPER.

The use of solutions of potassium permanganate as a disinfecting agent has been extensive and popular, from the standpoint of both efficiency and economy. Accurate details regarding the antiseptic and germicidal action of potassium permanganate upon *B. typhosus* seem to be lacking. Jäger's and Miquel's¹ statements are only approximate ones. Jäger says that a 5 per cent solution (approximately N/1.6) of potassium permanganate is a germicide to all pathogenic organisms, excepting tubercle bacillus, and that a 1 per cent solution (approximately N/0.32) is not reliable for the destruction of these same organisms. According to Miquel, potassium permanganate is an antiseptic in the proportion of 1:285 (approximately N/0.091).

Our preliminary experiments, made upon a pure 24-hour bouillon culture of *bacillus typhosus*, with dilute solutions of potassium permanganate, lead us to believe that the reagent is antiseptic and germicidal in less quantities than those given by Miquel and Jäger. The results of these preliminary experiments, therefore, occasioned the work of this introductory paper on the general subject of the germicidal action of potassium permanganate. We purpose to study closely the action of solutions of this reagent upon all of the common pathogenic organisms.

Methods.

In conducting the experiments all apparatus, including pipettes, burettes, test tubes, flasks, graduates, etc., was sterilized and all possible precautions were observed to avoid

¹ "Sternberg's Bacteriology," p. 186.

contamination. One-half liter quantities of sterile, distilled water, in sterile glass flasks, were used in the 8 series. Each series consisted of 2 flasks of sterile water, to each of which 1 cc. of a pure, 24-hour bouillon culture of *B. typhosus* was added, thus affording a means of checking results. Varying volumes of N/6000, N/4000, N/1000 and N/10 solutions of potassium permanganate were added to the several flasks containing the water and culture. The mixtures were incubated and, after varying periods of incubation, the ordinary methods were followed to determine the presence or absence of organisms.

EXPERIMENTAL PART.

In each of the 2 flasks of the 8 series given below, 500 cc. of sterile, distilled water were used, varying amounts of potassium permanganate solutions were added, as indicated for the different series, then 1 cc. of a pure 24-hour bouillon culture of *B. typhosus*, excepting in Series V. The temperature of the incubation was 37°.4 and the periods of growth were from 24-72 hours:

Series I.—Flasks (a) and (b), 25 cc. N/6000 potassium permanganate were added. Total volume, 526 cc.

Series II.—Flasks (a) and (b), 20 cc. N/4000 potassium permanganate were added. Total volume, 521 cc.

Series III.—Flasks (a) and (b), 20 cc. N/1000 potassium permanganate were added. Total volume, 521 cc.

Series IV.—Flasks (a) and (b), 10 cc. N/10 potassium permanganate were added. Total volume, 511 cc.

Series V.—Flasks (a) and (b), no potassium permanganate added. *Check flasks.* Total volume, 501 cc.

Series VI.—Flasks (a) and (b), 25 cc. N/6000 and 12.6 cc. N/10 potassium permanganate solutions were added. Total volume, 538.6 cc.

Series VII.—Flasks (a) and (b), 20 cc. N/4000 and 20.1 cc. N/10 potassium permanganate solutions were added. Total volume, 541.1 cc.

Series VIII.—Flasks (a) and (b), 20 cc. N/1000 and 50.3 cc.

Tabulation of Results.

Series.	Volume of permanganate.	Total volume.	Concentration of permanganate.	Growth checked.
I., <i>a</i> and <i>b</i>	25 cc. N/6000	526 cc.	N/126260	—
II., <i>a</i> and <i>b</i>	20 cc. N/4000	521 cc.	N/104200	—
III., <i>a</i> and <i>b</i>	20 cc. N/1000	521 cc.	N/26050	—
IV., <i>a</i> and <i>b</i>	10 cc. N/10	511 cc.	N/511	Growth inhibited, 67 colonies per cc. Check flasks, 4050 colonies per cc.
V., <i>a</i> and <i>b</i>	None	501 cc.		
VI., <i>a</i> and <i>b</i>	25 cc. N/6000 12.6 cc. N/10	538.6 cc.	N/426.6	
VII., <i>a</i> and <i>b</i>	20 cc. N/4000 20.1 cc. N/10	541.1 cc.	N/213.35	+
VIII., <i>a</i> and <i>b</i>	20 cc. N/1000 50.3 cc. N/10	571.3 cc.	N/113.06	+

N/10 potassium permanganate solutions were added. Total volume, 571.3 cc.

After all the flasks had remained in the incubator for 24 hours, tubes of sterile bouillon, 15 cc. each, were inoculated with 1 cc. from each flask. These bouillon tubes were incubated for 24 hours; cloudy growth was noted in all tubes of Series I., II., III. and V.; slower growth was shown, however, in the tubes inoculated with samples from Series IV., (a) and (b), and not until the end of 33 hours' incubation did these tubes show a uniform cloudy growth. Tubes from Series VI., VII. and VIII. remained clear after 48 and 72 hours' incubation. Three repetitions of these inoculations gave the same results.

Agar plates were inoculated with 1 cc. from flask (a), Series IV. After 48 hours' incubation the average colony count showed 67 per cc.

An agar plate was inoculated with 1 cc. from flask (a), Series V. After 32 hours' incubation 4050 colonies per cc. were estimated.

In the above experiments all cultures were studied in regard to morphology and cultural characters and no contaminations were observed.

The results obtained from the flasks of Series IV. indicate that N/511 potassium permanganate is antiseptic to *B. typhosus*.

The mixtures in the flasks resulting from experiments, Series VI. to VIII., inclusive, were of a rose color, thus indicating an excess of permanganate. An excess of 0.00245 gram permanganate was found in flasks (a) and (b) of Series VI., by titration with standard ferrous ammonium sulphate solution, in presence of dilute sulphuric acid. This excess, deducted from the total quantity added, left the amount of permanganate which was germicidal to *B. typhosus*. The concentration calculated is N/458.

Contributions from the Chemical Laboratory of Harvard College.

ON ORTHOPARADIBROMORTHOPHENYLENEDIAMINE.

BY C. LORING JACKSON AND F. W. RUSSE.

The substance described in this paper was prepared in the hope that a diamine containing bromine might convert tetrabromorthoquinone into a quinoxaline, but it acted no better than the orthophenylenediamine itself, giving, like that, red amorphous products, which we think were formed by oxidation of the amino groups.

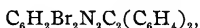
We tried first to make the tetrabrom derivative by the action of bromine on orthophenylenediamine, but could obtain only red amorphous substances, which we think are identical with those mentioned in the preceding paragraph. We next prepared the 2,4-dibromorthonitraniline of Remmers,¹ reduced it to the new orthoparadibromorthophenylenediamine and tried the action of bromine on this, but with similar bad results. Accordingly, we gave up the attempt to make the tetrabrom compound and studied the orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$, obtained as described above. This melts at 83° and, therefore, has the constitution $NH_2 = 1,2$; $Br_2 = 4,6$, as the 4,5-dibromorthophenylenediamine, melting at 137° , has been made by Schiff,² and the only other possible isomer, 3,6-dibromorthophenylenediamine, melts at $94^\circ-95^\circ$, and was made by Calhane and Wheeler.³

With hydrochloric acid the orthoparadibromorthophenylenediamine gave a monohydrochloride, $C_6H_2Br_2(NH_2)NH_3Cl$, stable in the air but decomposed by hot water, whereas with hydrobromic acid, under the same conditions, a dihydrobromide, $C_6H_2Br_2(NH_3Br)_2$, seemed to be formed, which was so unstable that we did not succeed in obtaining it in a state of purity. Acetic anhydride converted our diamine into the diacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$, which melts at $227^\circ-228^\circ$. With phenanthrenequinone it formed the quinoxaline,

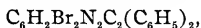
¹ Ber. d. chem. Ges., **7**, 349 (1874).

² Sitzun. Wien., **99**, 2b, 361 (1890).

³ THIS JOURNAL, **22**, 452 (1899).



which melts at 248° , whereas Schiff's 4,5-compound melts at 286° and Calhane and Wheeler's 3,6-body at 297° . With benzil our dibromorthophenylenediamine gave



melting at 149° – 150° , the 3,6-compound melts at 215° – 216° .

Hinsberg¹ found that diphenylenequinoxaline itself gave a deep red color with all the strong mineral acids; our two quinoxalines gave such a color with strong sulphuric acid, but were not turned red by strong hydrochloric acid or nitric acid, although the phenanthrene compound was reddened by fuming nitric acid. The dibromquinoxalines of Calhane and Wheeler² behaved like ours in regard to acids.

The replacement of bromine by hydrogen during the reduction of aromatic compounds with tin and hydrochloric acid has been observed³ in many cases, but in all of these the groups containing nitrogen were in the meta position to each other with two exceptions, one of which was the reduction of symmetrical tribromaniline to dibromaniline⁴ and the other the formation of a small quantity of orthophenylenediamine from parabromorthonitraniline, observed by Hübner.⁵ As the yield of our dibromorthophenylenediamine was very small, we thought it possible that such a reaction might have taken place, but a careful search failed to show orthophenyldiamine in our reduction product. We confirm, therefore, the results previously obtained and it is evident that ortho-nitro compounds have little tendency to lose bromine under the action of tin and hydrochloric acid.

EXPERIMENTAL.

The 2,4-dibrom-6-nitraniline was prepared by adding bromine, diluted with a little acetic acid, to a solution of ortho-nitraniline in 10 times its weight of acetic acid, in the proportion of

¹ Ann. Chem. (Liebig), **237**, 340 (1887).

² THIS JOURNAL, **22**, 457 (1899).

³ Jackson and Calvert: *Ibid.*, **18**, 465 (1896).

⁴ *Ibid.*, **18**, 480 (1896).

⁵ Ann. Chem. (Liebig), **209**, 360 (1881).

2 molecules of bromine to 1 of the base. The bromine disappeared instantly, with a slight evolution of heat. The product was precipitated by the addition of water and, after a thorough washing, recrystallized once from dilute alcohol, which raised the melting point to 127° , that observed by Remmers.¹ The yield was quantitative.

An excess of bromine gave no further action, even when the mixture was boiled for 5 hours in a flask with a return condenser.

Preparation of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$.—The reduction of the 2,4-dibrom-6-nitraniline was effected most conveniently with tin and hydrochloric acid, as this gives a white product, whereas zinc and acetic acid frequently give a brownish diamine, which, however, is essentially pure, as it melts at the same point as the white one.

The dibromnitraniline, moistened with a little alcohol, was warmed with 50 times its weight of hydrochloric acid and an excess of tin in a flask, on the steam-bath, until the yellow color of the nitraniline had disappeared. An excess of potassic hydrate was then added and the solution distilled, when the dibromorthophenylenediamine passed over. As the water distilled off more was added, taking care not to dilute the solution too much, since the diamine does not begin to volatilize until the boiling point of the solution reaches 123° . The product obtained in this way was pure. The diamine was also prepared by reduction with zinc and acetic acid, which had the advantage that it was not necessary to isolate the solid dibromnitraniline, but finely granulated zinc could be added directly to the acetic acid solution in which the dibrom product was formed. If the solid nitraniline was used, 5 grams of it were mixed with 50 grams of glacial acetic acid and an excess of finely granulated zinc, water was then added until there was an active evolution of hydrogen and the mixture allowed to stand over night at 60° – 70° . The product, disregarding any crystals of zincic acetate which had separated, was treated with an excess of sodic hydrate and distilled, as already described. The yield by either

¹ Ber. d. chem. Ges., 7, 349 (1874).

process was about 5 per cent of the weight of the dibromni-traniline. Some of the diamine filtered from the distilled water was dried in a desiccator for analysis :

0.1547 gram substance gave 0.2177 gram AgBr.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	59.89

Properties of Orthoparadibromorthophenylenediamine.—It crystallizes from dilute alcohol in small, slender, colorless prisms, which turn dark on exposure to the air. As obtained by distillation with steam, it forms a mat of long, fine needles. It crystallizes from ligroin in radiating needles, from hot water in rhombic plates. It melts at 83° to a colorless liquid. It is freely soluble in alcohol ; soluble in ether, benzene, acetone, chloroform, carbonic disulphide, or glacial acetic acid ; less soluble in ligroin ; slightly soluble in hot water. All its solutions turn dark on exposure to the air. It dissolves in strong, hot hydrochloric acid, forming a hydrochloride, which crystallizes out in transparent needles. Strong, hot hydrobromic acid also dissolves it and deposits a hydrobromide in short prisms. Strong nitric acid gives a red solution with it, from which nothing is precipitated on dilution, but if dilute nitric acid is used the solution has a deeper red color, and addition of water throws down an amorphous, brownish red precipitate. Cold, strong sulphuric acid dissolves it and on dilution clusters of flat, transparent prisms are deposited. Alkalies have no effect on it.

Hydrochloride of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2NH_3Cl$.—This salt was most easily prepared by passing a stream of dry hydrochloric acid gas into a solution of the diamine in dry benzene. The hydrochloride was thrown down as a pink, gelatinous precipitate, which was dried over soft paraffin and potassic hydrate for analysis :

0.1385 gram substance gave 0.2374 gram AgBr + AgCl.

	Calculated for $C_6H_2Br_2(NH_2)_2HCl$.	Found.
Br + Cl	64.97	64.48

The pink precipitate analyzed was seen under the microscope to consist of very fine needles. It was decomposed by hot water or alkalis.

Dihydrobromide of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_3Br)_2$.—When hydrobromic acid gas was passed through a solution of the diamine in dry benzene, a precipitate was obtained which probably was the dihydrobromide, but lost hydrobromic acid so easily that we were unable to get a good analysis of it. The specimens for Analyses I. and II. were dried by pressing between filter paper, III. by heating to constant weight at 95° , IV. by drying at 90° in a current of dry hydrobromic acid.

I. 0.1511 gram substance gave 0.2623 gram AgBr.

II. 0.1587 gram substance gave 0.2721 gram AgBr.

III. 0.1585 gram substance gave 0.2678 gram AgBr.

IV. 0.2672 gram substance gave 0.4498 gram AgBr.

	Calculated for		I.	Found.		
	$C_6H_2Br_2(NH_2)_2HBr$.	$C_6H_2Br_2(NH_3Br)_2$.		II.	III.	IV.
Br	69.13	74.74	73.87	72.97	71.90	71.64

The salt, therefore, loses hydrobromic acid even in an atmosphere of this gas. It is decomposed by hot water or alkalis.

Orthoparadibromorthophenylenediacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.—Half a gram of the dibromorthophenylenediamine was boiled for 15 minutes with acetic anhydride, and as the colorless solution deposited nothing on cooling, water was added, which threw down a white, flocculent precipitate. We did not succeed in finding a solvent from which this substance could be recrystallized in the ordinary way; it was, accordingly, purified by making a dilute solution in acetic acid and allowing this to stand under a bell jar, over night, with a strong solution of ammonia. As the acetic acid was neutralized by the ammonia gas, the new compound crystallized out in long needles, and two such crystallizations were sufficient for complete purification. It was dried at 95° for analysis:

0.1000 gram substance gave 0.1071 gram AgBr.

	Calculated for $C_6H_2Br_2(NHC_2H_5O)_2$.	Found.
Br	45.66	45.58

Properties.—It crystallizes in long, white needles, which melt at 227° – 228° . It is soluble in ethyl or methyl alcohol, acetone, chloroform, or acetic acid; sparingly soluble in benzene or ligroin. We could not obtain crystals from any of these solutions by the usual methods. It dissolves in strong hydrochloric acid, but is precipitated on dilution; it is soluble in strong nitric acid, strong sulphuric acid, or an excess of hot sodic hydrate solution.

Orthoparadibromdiphenylenequinoxaline (*Orthoparadibromphenanthrophenazine*), $C_6H_2Br_2N_2C_2(C_6H_4)_2$.—Two-tenths gram of the dibromphenylenediamine were dissolved in alcohol and mixed with an acetic acid solution of 0.15 gram of phenanthrenequinone; a heavy precipitate, made up of fine, yellowish needles, was deposited at once, which was so pure that one recrystallization from benzene was sufficient to raise it to the constant melting point, 248° . It was dried at 95° for analysis:

0.1343 gram substance gave 0.1148 gram AgBr.

	Calculated for $C_6H_2Br_2N_2C_{14}H_8$.	Found.
Br	36.51	36.38

Properties.—It crystallizes from benzene in silky, yellow needles, arranged in radiating groups, which melt at 248° . It is soluble in hot benzene or chloroform, sparingly in cold; very slightly soluble in alcohol, ether, acetone, or glacial acetic acid; insoluble in ligroin or water. Strong hydrochloric acid turns it slightly yellow; strong nitric acid has no effect, but fuming nitric acid gives a red solution; strong sulphuric acid forms a deep red solution with it. Alkalies do not act on it.

Orthoparadibromdiphenylquinoxaline, $C_6H_2Br_2N_2C_2(C_6H_5)_2$.—A solution of 0.15 gram of benzil, in 10 cc. of alcohol, was boiled for 1 hour with 0.2 gram of the dibromphenylenediamine. As the solution cooled white needles were deposited which, after 2 recrystallizations from dilute alcohol, showed

the constant melting point 149° – 150° and were dried at 95° for analysis :

0.1565 gram substance gave 0.1337 gram AgBr.

	Calculated for $C_6H_2Br_2N_2C_2(C_6H_5)_2$.	Found.
Br	36.36	36.37

Properties.—It crystallizes from dilute alcohol in long, white needles, which melt at 149° – 150° . It is soluble in alcohol, ether, chloroform, benzene, acetone, hot methyl alcohol, or hot glacial acetic acid ; insoluble in ligroin or water. It is slightly soluble in strong hydrochloric acid ; hot, strong nitric acid converts it into a pale yellow solution and an oil, on dilution with water a white precipitate is formed ; cold, strong sulphuric acid forms with it a blood-red solution, from which water precipitates a white solid. Alkalies have no effect on it.

When the orthoparadibromophenylenediamine was treated with tetrabromorthobenzoquinone, a red, slightly tarry mass was formed, from which we have not succeeded in isolating any definite compound.

CAMBRIDGE, MASS.,
Sept. 12, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.¹

BY C. LORING JACKSON AND F. W. RUSSE.

In this paper we describe a continuation of the investigation of tetrabromorthobenzoquinone, $C_6Br_4O_2$, which has been carried on for some years in this laboratory.²

We turned our attention in the first place to the action of ketones on tetrabromorthobenzoquinone, as preliminary experiments had shown that these substances reacted even in the cold and Japp found that acetone³ or acetophenone⁴ combines

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Frederick W. Russe.

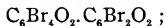
² Jackson and Koch : *THIS JOURNAL*, **26**, 10 (1901). Jackson and Porter : *Ibid.*, **30**, 518 (1903) ; **31**, 89 (1904). Jackson and Carlton : *Ibid.*, **34**, 422 (1905).

³ Japp and Streatfield : *J. Chem. Soc.*, **41**, 274 (1882).

⁴ Japp and Meldrum : *Ibid.*, **75**, 1034 (1899).

with phenanthrenequinone, while Klinger¹ has obtained addition compounds of aldehydes with it. It seemed probable, therefore, that our orthobenzoquinone would give, under these conditions, series of compounds similar to those formed by the action of alcohol on it.² Porter and one³ of us, in fact, had found that acetophenone combined with tetrabromorthoquinone in the cold, forming an unstable addition product, which may be considered to be the quinone with 1 mol. of acetophenone of crystallization. On longer standing with acetophenone a yellow product was formed, the nature of which was not determined. When the substances were boiled together the bromine compounds were broken up in great measure and the hydrobromic acid formed converted part of the acetophenone into triphenylbenzene.

Of the ketones studied by us, benzophenone was the only one that did not act on tetrabromorthoquinone in the cold, and even from this we obtained an action if it was dissolved in chloroform, but we are inclined to ascribe this to the solvent, as there was no action when benzene was used. Acetone, diethylketone, mesityl oxide, or acetophenone reacted easily with the tetrabromorthobenzoquinone, but to our great disappointment, instead of forming addition compounds the same products were formed in each case. These were three in number: the red hexabromorthoquinopyrocatechin ether,⁴



brown hexabromdihydroxy pyrocatechin ether,⁵



and a new yellow compound, identified as heptabromorthoquinopyrocatechin hemiether, $\text{C}_6\text{Br}_4(\text{OH})\text{OC}_6\text{Br}_2\text{O}_2$. By regulating the conditions of the reaction each of these compounds can be made the principal product; thus with half its weight of acetone, best diluted with benzene, the tetrabromorthoquinone gave the heptabrom compound almost pure; with twice

¹ Ann. Chem. (Liebig), **249**, 138 (1888).

² THIS JOURNAL, **31**, 89 (1904).

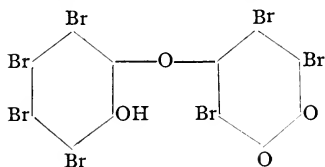
³ *Ibid.*, **31**, 116 (1904).

⁴ *Ibid.*, **26**, 35 (1901).

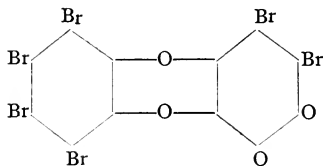
⁵ *Ibid.*, **26**, 38 (1901).

its weight of acetone the hexabromorthoquinopyrocatechin ether was formed at first, which on longer standing, went almost completely into the dihydroxy compound. Shining brassy scales were also observed frequently among the products of the reaction, but these, by continuous extraction with benzene, yielded the two hexabrom ethers and probably, therefore, consisted of a mixture or loose compound of these two substances.

The constitution of the heptabromorthoquinopyrocatechin hemiether, I., was determined by the following observations:¹



I.



II.

It passed into the hexabrom ether, II., with great ease, when treated with acetone, dilute alcohol, dilute acids, or even when exposed to the air. It must contain quino oxygens, because nitric acid did not act on it, as would have been the case if it were a trihydroxy compound; and benzoyl chloride gave a derivative analyzing nearly for $C_{12}Br_7O(OCOC_6H_5)_3$, while at the same time a brown gas was given off which bleached moist litmus paper. Graebe² and H. Schulz³ have shown that acetyl chloride or bromide acts on paraquinones in a similar way, giving a hydroquinone diacetate and chlorine or bromine, which

¹ A possible formula isomeric with I. is discussed later.

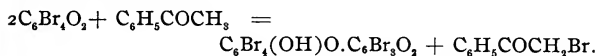
² Ann. Chem. (Liebig), 146, 13, 23 (1869).

³ Ber. d. chem. Ges., 15, 652 (1882).

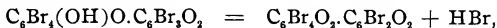
is afterward used up, more or less completely, by secondary reactions. In our case, the chlorine formed in this way displaced part of the bromine in the heptabrom compound. An experiment with tetrabromorthoquinone itself gave confirmatory results, as, when treated with benzoyl chloride, it gave a brown gas, probably a mixture of bromine and chlorine, and a product containing the percentage of Br for the formula $C_6Br_4(OCOC_6H_5)_2$, but which melted at $172^\circ-174^\circ$ instead of at 197° , the melting point of the tetrabromopyrocatechin dibenzoate, which was made for comparison. We cannot explain this difference of 25° in the melting points.

In addition to the three derivatives of the quinone already mentioned there was formed in every case a bromketone, as was unpleasantly evident by its violent action on the eyes. With acetophenone the compound formed was the ω -bromacetophenone, $C_6H_5COCH_2Br$, which we proved by converting it into ω -anilinoacetophenone, $C_6H_5COCH_2NC_6H_5$, melting at 94° .

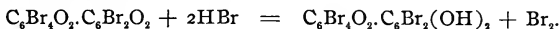
The reaction by which the yellow hemiether was formed can be written as follows :



The red hexabrom ether would, later, be formed from this,



and the brown dihydroxy ether would result from the reducing action of the hydrobromic acid :



The free bromine would then act on the excess of the ketone to give more hydrobromic acid for this last reaction.

That the hexabromorthoquinopyrocatechin ether,



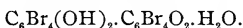
could be reduced by hydrobromic acid to the dihydroxy ether, as in the last reaction, was shown by a special experiment, in which it was treated with acetone and bromine. In this work the dihydroxy body was obtained either in brown plates looking like mica, or in white, fibrous needles like asbestos, and it

was proved that the two products were identical in spite of the difference in their appearance.¹

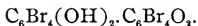
If bromine was added to a mixture of acetone and tetrabromorthoquinone the action seemed to be much more rapid and ran further than when acetone was used alone. This was obviously due to the reducing action of the hydrobromic acid formed, which converted part of the quinone to tetrabrompyrocatechin, and this, reacting with unaltered quinone, formed the hemiether or ether. If the mixture was diluted with benzene, the reduction ran so far that tetrabrompyrocatechin was one of the products of the reaction.

The action of tetrabromorthoquinone with oenanthal or with benzaldehyde gave the red and yellow products obtained by the action of ketones. Under these circumstances it did not seem worth while to multiply experiments with aldehydes.

In his paper² on tetrabromorthoquinone, Zincke mentions a black substance, which he took for the quinhydrone, but he did not study it in detail. Koch and one of us³ did not succeed in making this compound, but we have found that it is formed whenever hot solutions of the tetrabromorthoquinone and tetrabrompyrocatechin, in equivalent amounts, are mixed and allowed to cool at once. Chloroform is the best solvent for this purpose. The shining, black crystals obtained in this way gave analytical results agreeing with the formula



As this formula rests on six analyses of different specimens, there can be no doubt that the substance is not



That the low result was not due to a loss of hydrobromic acid was shown by a special experiment, and therefore it follows that it must be caused by the addition of some substance to the quinhydrone, which can only be water, since the same product was obtained with chloroform or benzene. Such a strong tendency to combine with water was observed by Porter and one

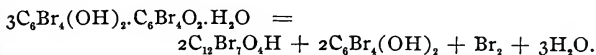
¹ Cf. similar observations of Shaffer.

² Ber. d. chem. Ges., **20**, 1778 (1887).

³ THIS JOURNAL, **26**, 37 (1901).

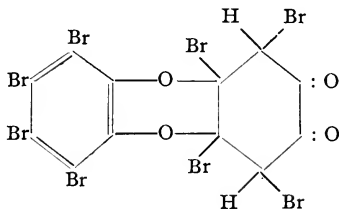
of us¹ with the tetrabromorthoquinone. An attempt to obtain a similar addition with isoamyl alcohol gave only the water compound.

A series of synthetic experiments showed that the substance contained 1 molecule of the tetrabromorthoquinone combined with 1 of tetrabrompyrocatechin. Our reasons for considering it a quinhydrone are its formation from the orthoquinone and pyrocatechin, its marked color and its composition, apart from the unexplained molecule of water. Its behavior with solvents, on the other hand, at first sight seems different from that of the paraquinhydrone, since it is converted with great ease into the heptabrompyrocatechin hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, and tetrabrompyrocatechin. It is possible, however, that this change is preceded by a dissociation into its components similar to that observed with paraquinhydrone. In the decomposition with boiling benzene the change was followed quantitatively and was found to correspond to the reaction:



The same reaction took place when the dry quinhydrone was heated.

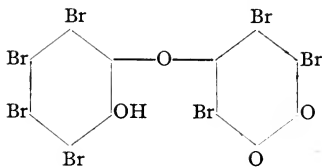
If, as we think, our substance is the orthoquinhydrone, it should have the graphical formula III., according to the constitution established by Posner² for the para compound:



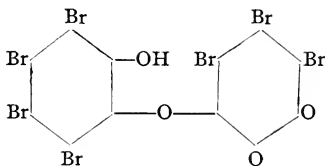
III.

¹ THIS JOURNAL, 31, 109 (1904).

² Ann. Chem. (Liebig), 336, 85 (1904).



I.



IV.

We give only the keto form, as it seems to us the strong color of the quinhydrones renders Posner's enol formula improbable. In this discussion we have omitted the molecule of water, as we have no experimental evidence to show how it is attached to the molecule.

If the heptabrom hemiether is formed from the undissociated quinhydrone, Formula I. must be the correct one for it, as a substance having Formula IV. could not be formed from III. without dissociation, but, as we have pointed out already, the analogy with the para compound would lead us to expect a complete dissociation of the quinhydrone in its solutions, so that this argument is entitled to but little weight.

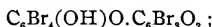
We have devoted a great deal of time to the study of the action of acetic acid on tetrabromorthoquinone, but, although our results explain one of the reactions which takes place, they are not in harmony with those of our predecessors. Koch,¹ by the long-continued action of warm acetic acid on tetrabromorthoquinone, obtained, without difficulty, a white product melting at 230° without visible decomposition,² and giving

¹ THIS JOURNAL, 26, 42 (1901).

² This fact was verified by taking the melting point of a specimen of the substance left from Koch's work.

analytical results corresponding to the formula $C_{14}H_2Br_8O_6$. Porter,¹ who took up the work later, could not obtain this substance, but found instead a yellowish product resembling heptabromorthoquinopyrocatechin hemiether in appearance, but melting, with decomposition, at 220° – 230° , instead of at 244° – 245° and containing 3.5 per cent less bromine. Our attempts to prepare Koch's products were even less successful as, when we followed most carefully the directions given by him, we obtained nothing but the red hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2 \cdot C_6Br_2O_2$. Three different men, therefore, have obtained three different results from the same process, showing that slight and apparently trifling differences in the conditions must have a marked effect on the product.

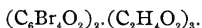
In other experiments the method of Koch was somewhat modified. For instance, we replaced with benzene the acetic acid or the alcohol and acetic acid used by Koch in purifying this compound and, in both cases, obtained the same substance, which crystallized in yellow needles and melted, with decomposition, between 235° and 250° . Another experiment, in which the heating of the tetrabromorthoquinone with acetic acid at 100° was continued much longer, yielded nearly pure heptabromorthoquinopyrocatechin hemiether,



and, when the materials were boiled together for 7 hours instead of being heated only at 100° , some tetrabrompyrocatechin was detected in the product.

We have also studied the action of acetic acid on tetrabromorthoquinone in the cold. Porter obtained, in a preliminary experiment of this sort, 2 products, one white melting at 85° – 90° without apparent decomposition, the other pinkish white, melting between 90° and 110° , but he made no attempt to purify either of them. In the many experiments tried by us we have found no indications of these substances, but instead have obtained only nearly square, thick, rhombic plates, which redden when heated, but do not melt under 300° . They gave results on analysis corresponding to the formula

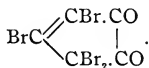
¹ THIS JOURNAL, 31, 114 (1904).



As they had no melting point, and could be recrystallized only with great difficulty, it is not certain that the specimen analyzed was pure, but it seems hardly probable that any large amount of impurity could be present in such well formed crystals.

If this substance was crystallized 10 times from benzene it was converted into the yellow needles, melting, with decomposition, at 235° – 250° , obtained by the action of hot acetic acid; and the same compound was also formed by the action of formic acid on tetrabromorthoquinone. As this same product has been made by 3 methods from acetic acid and also from formic acid, we feel there is no doubt that it is a definite compound, in spite of the wide range of its decomposition temperature. Its analysis indicates that it is the ether or oxide corresponding to the heptabromorthoquinopyrocatechin hemiether, that is, $(\text{C}_6\text{Br}_4\text{O} \cdot \text{C}_6\text{Br}_3\text{O}_2)_2\text{O}$, and it may be called, therefore, diheptabromorthoquinopyrocatechin ether. A specimen of the substance, crystallized 12 times from benzene, seemed to be partially converted into the hemiether, $\text{C}_6\text{Br}_4(\text{OH})\text{O} \cdot \text{C}_6\text{Br}_3\text{O}_2$, a result in harmony with our theory of its constitution, but other confirmatory results must be discovered before the formula can be considered finally established. The action of propionic, butyric, or valerianic acids on tetrabromorthoquinone gave what seemed to be the same compound in a somewhat impure state.

Some attempts to make bromine addition products of tetrabromorthoquinone did not lead to the desired result, but in the course of this work we boiled it with fuming nitric acid and bromine and obtained 2 new compounds, a white acid soluble in water, and a yellow substance melting, without decomposition, at 142° , which gave analytical results corresponding to the formula $\text{C}_5\text{Br}_4\text{O}_2$. Upon treating this substance with orthodiamines, products were obtained which gave, with sulphuric acid, the deep red color characteristic of quinoxalines of this class. We feel justified, therefore, in considering it, for the present, the tetrabromcyclopenteneorthoquinone,



Unfortunately, this product and the white acid were discovered too late in the year for thorough study. The investigation of both will be continued in this laboratory in the coming academic year.

EXPERIMENTAL.

The tetrabromorthoquinone used in this work was prepared by the method described by Koch and one of us,¹ with the improvements introduced by Shaffer,² except that less care was taken in cooling the oxidation mixture both before the oxidation and after the addition of water; 30 grams of tetrabrompyrocatechin yielded in this way 24 grams of the orthoquinone, melting at 149°–150°.

Action of Cold Acetone on Tetrabromorthoquinone.

Our preliminary experiments showed that there were three products of this action, a yellow, a red and a brown, any one of which could be obtained as the principal product by a careful adjustment of the conditions.

The Red Product.—The best way to obtain this substance was to allow 5 grams of tetrabromorthoquinone to stand at ordinary temperatures, in a corked flask, with 10–15 grams of pure, anhydrous acetone. During the first 4 or 5 days the product was deposited in small, red prisms, and if these were filtered out each day, the yield varied from 50 to 65 per cent of the quinone used. The yield depended on the amount of acetone, as, if the quinone was treated with half its weight of acetone, very little of the red product was formed, and with its own weight only 10–15 per cent of the weight of the quinone was obtained. The crystals as deposited from the acetone solution were often of good size, and showed the form characteristic of the hexabromorthoquinopyrocatechin ether

¹ THIS JOURNAL, 26, 34 (1901).

² *Ibid.*, 34, 460 (1905).

discovered by Koch and one of us.¹ That it was this compound was shown by its other properties—infusibility even at 300° and essential insolubility in all solvents except nitrobenzene—and by the following analyses of the substance made without recrystallization, which accounts for the somewhat high percentages. Each specimen used proceeded from a different preparation.

- I. 0.2688 gram substance gave 0.4447 gram AgBr.
 II. 0.2175 gram substance gave 0.3589 gram AgBr.
 III. 0.2196 gram substance gave 0.3628 gram AgBr.

	Calculated for $C_6Br_4O_2 \cdot C_6Br_2O_2$.	I.	Found. II.	III.
Br	69.76	70.42	70.23	70.33

In this and all the actions of acetone with the quinone, bromoacetone was formed as a secondary product, and to avoid its irritating effect on the eyes it must be removed by allowing the crystals to stand under a good hood before studying them.

The Brown Product.—This substance is the final product of the action of acetone on tetrabromorthoquinone. If, therefore, a mixture of 5 grams of the quinone with 10 cc. of acetone, such as that mentioned in the last section, was allowed to stand more than 5 days, the red crystals, and some glittering yellow plates, which were also formed, were converted, in a few days more, into long, brownish black needles, the solution turning from red to straw color.

The brown compound was also formed by the further action of acetone on the red hexabromorthoquinopyrocatechin ether. It is nearly insoluble in the common solvents except alcohol, in which it is very slightly soluble. From this it crystallizes in slender, white needles, which mat together like asbestos. Nitrobenzene dissolves it freely and it crystallizes from this solution in mica-like plates, apparently hexagonal in form and of a pale brown color, or, if crystallized very slowly, in white needles. It decomposes at 304°–305°. Sodid hydrate, in aqueous solution, does not dissolve it, but sometimes turns the white needles purple. These properties indicate that the sub-

¹ THIS JOURNAL, 26, 36 (1901).

stance is the hexabromdihydroxyprocatechin ether¹ and this was confirmed by the following analysis of the substance recrystallized from nitrobenzene :

0.2669 gram substance gave 0.4370 gram AgBr.

	Calculated for $C_6Br_4O_2.C_6Br_2(OH)_2$.	Found.
Br	69.56	69.68

The glittering yellow plates mentioned above appeared almost invariably as an intermediate product in the action of acetone on tetrabromorthoquinone ; they had a brassy color and luster and looked not unlike bronze powder. On treatment with benzene, in a continuous extractor, they were converted into the red and brown products described above. Longer standing with acetone changed them completely into the hexabromdihydroxyprocatechin ether.

The Yellow Product. Heptabromorthoquinopyrocatechin Hemither, $C_6Br_4(OH)O.C_6Br_3O_2$.—This substance was made by mixing 5 grams of tetrabromorthoquinone with 2.5 grams of acetone and allowing the damp powder to stand in a corked flask. In 24–48 hours the solid began to swell up, as lime does in slaking, and was converted into an amorphous pink mass, which, after standing another day, had crystallized in small needles and consisted principally of the yellow compound, nearly free from the brown or red substance. This product was first allowed to stand in a current of air, until the bromacetone had evaporated. It was then extracted with benzene and purified by repeated crystallization from this solvent.

An even purer product was obtained by the following method : One gram of the tetrabromorthoquinone was mixed with 0.5 gram of pure acetone, dissolved in 10 grams of benzene, and the mixture was allowed to stand at ordinary temperatures in a corked flask. For 10 days there was no sign of a reaction, but after that time the solution began to take on a straw-yellow color, and at the end of 2 weeks deposited yellow crystals, which were nearly pure. They were freed from

¹ THIS JOURNAL, 26, 39 (1901).

bromacetone and purified as before. The yield was 70 per cent of the quinone used. Most of the substance used by us was prepared by this method. A specimen recrystallized from benzene, until it showed the constant decomposition point 244° – 245° , was carefully dried between filter papers for analysis :

I. 1.2158 grams substance, heated at 90° – 95° , lost 0.1650 gram C_6H_6 .

II. 0.5553 gram lost 0.0735 gram C_6H_6 .

III. 0.5109 gram lost 0.0684 gram C_6H_6 .

	Calculated for $C_6Br_4(OH)O.C_6Br_3O_2.1\frac{1}{2}C_6H_6$.	I.	Found. II.	III.
C_6H_6	13.22	13.57	13.23	13.39

I. 0.4051 gram substance, dried at 90° – 95° , gave 0.2714 gram CO_2 and 0.0148 gram H_2O .

II. 0.3214 gram substance gave 0.5520 gram AgBr (Carius).

III. 0.3155 gram substance gave 0.5412 gram AgBr.

	Calculated for $C_6Br_4(OH)O.C_6Br_3O_2$.	I.	Found. II.	III.
C	18.73	18.27
H	0.13	0.41
Br	72.80	. .	73.10	73.02

Properties of Heptabromorthoquinopyrocatechin Hemiether.—Crystallized from benzene, it formed large square plates or thick, square prisms, of a full yellow color, which effloresce on exposure to the air. When heated it turns orange between 200° and 240° , and at 244° – 245° melts to a deep red liquid with great increase in volume and evolution of a little reddish gas. It is soluble in hot benzene, chloroform, ether, or nitrobenzene; essentially insoluble in ligroin. Ethyl alcohol dissolves it, but if the solution is heated, even by holding the vessel in the hand, decomposition sets in as shown by the formation of a red precipitate of hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$. Methyl alcohol acts in the same way, but more slowly. It is also converted into the hexabrom ether by long exposure to the air, by the action of dilute acids, by acetic anhydride, or acetyl chloride, or by standing at ordinary temperatures with acetone for a month;

in this last case the action goes further, as part of the hexabrom ether is converted into the brown hexabromdihydroxypyrocatechin ether, $C_6Br_4O_2.C_6Br_2(OH)_2$. Strong or fuming nitric acid apparently did not act on it. Sodid hydrate decomposed it, dissolving part of it and leaving the rest in the form of a black, amorphous mass.

Reduction of Heptabromorthoquinopyrocatechin Hemiether.—

An attempt to reduce this substance with sodium amalgam failed, because of the formation of the black product of the action of sodid hydrate.

With zinc and dilute acetic acid a flocculent, purple-brown substance was obtained, which was recognized as hexabromdihydroxypyrocatechin ether by the following properties: It decomposed at 306° – 307° ; crystallized from hot alcohol, in which it was very sparingly soluble, in white, asbestos-like needles; from hot nitrobenzene in plates or needles; it was essentially insoluble in the other common solvents except benzene, in which it is slightly soluble. Benzoyl chloride converted it into a white ether. One gram of the heptabrom ether gave 0.6 gram of the hexabrom ether, or 67 per cent of the theoretical yield.

Phenylhydrazine, in benzene solution, also converted the heptabrom hemiether into the hexabromdihydroxy ether, which, in this case, appeared in pink plates looking like mica and was recognized by its properties. It was mixed with white needles of phenylhydrazine hydrobromide.

Tribenzoylheptabromdihydroxypyrocatechin Hemiether,

$C_6Br_4(OCOC_6H_5)O.C_6Br_2(OCOC_6H_5)_2$.—Although acetyl chloride gave the hexabrom ether, benzoyl chloride converted the heptabromorthoquinopyrocatechin hemiether into its tribenzoyl derivative. For this purpose 4 grams of the hemiether were boiled with 10 grams of benzoyl chloride, for 1 hour. The red solution at first gave off red fumes which bleached moist litmus paper and, therefore, contained bromine, probably mixed with chlorine. After 10 or 15 minutes the evolution of these fumes ceased, and at the end of the hour the solution, on cooling, deposited a white, crystalline mass, which was washed

thoroughly with hot water to remove benzoyl chloride, and then crystallized repeatedly from benzene until it showed the constant melting point 294° – 296° , when it was dried at 95° for analysis. The specimen used for the combustion was boiled a second time with benzoyl chloride and purified as before.

I. 0.3098 gram substance gave 0.4042 gram CO_2 and 0.0382 gram H_2O .

II. 0.2484 gram substance gave 0.3072 gram AgBr.

	Calculated for $\text{C}_6\text{Br}_4(\text{OCOC}_6\text{H}_5)\text{O} \cdot \text{C}_6\text{Br}_3(\text{OCOC}_6\text{H}_5)_2$	I.	Found.	II.
C	36.56	35.58	.	.
H	1.38	1.38	.	.
Br	51.71	.	.	52.62

These results seem to indicate that our product contained an impurity of a dibenzoyl compound, but the case is probably not so simple as this, since bromine was given off in the formation of the substance and, therefore, the chlorine set free by the action of the quinone on benzoyl chloride must have replaced the bromine in part of the hemiether, although, as the analyses show no trace of the presence of a chlorine compound, this must have been removed by the recrystallization.

Properties of the Tribenzoyl Compound.—It crystallizes from benzene in small, flat, transparent plates, which melt at 294° – 296° , apparently without decomposition. This somewhat indefinite melting point is in accord with our theory that the substance was contaminated with the dibenzoyl compound. It is soluble in benzene or nitrobenzene; sparingly soluble in alcohol; essentially insoluble in ligroin or water.

Action of Benzoyl Chloride on Tetrabromorthoquinone.—Eight grams of the quinone were boiled for 2 hours with 20 grams of benzoyl chloride. The solution at first was red and gave off red vapors which bleached moist litmus paper, but after 10 minutes boiling the red vapors ceased to appear and the liquid had become colorless. Nothing separated on cooling, therefore the benzoyl chloride was distilled off with steam and the white crystalline residue, well washed with hot water, was purified by recrystallization from a mixture of 1 part of ben-

zene and 2 of ligroin until it showed the constant melting point 172° – 174° , when it was dried at 95° for analysis.

0.2266 gram substance gave 0.2665 gram AgBr.

	Calculated for $C_6Br_4(OCOC_6H_5)_2$.	Found.
Br	50.47	50.05

This analysis would make the substance tetrabrompyrocatechin dibenzoate, but it melted at 172° – 174° , whereas the real melting-point of this compound is 197° , as shown in the following section. This large difference in the melting point would indicate a larger amount of impurity than is shown by the analysis, so that we are unable to account for this anomaly, which is rendered still more puzzling by the facts that the melting point, 172° – 174° , although not sharp, was constant and the crystals appeared homogeneous under the microscope.

Dibenzoate of Tetrabrompyrocatechin, $C_6Br_4(OCOC_6H_5)_2$.—Five grams of tetrabrompyrocatechin were heated for 7 hours with 10 grams of benzoyl chloride. The product was purified as described in the preceding section, and showed the constant melting-point 197° .

0.1814 gram substance gave 0.2153 gram AgBr.

	Calculated for $C_6Br_4(OCOC_6H_5)_2$.	Found.
Br	50.47	50.52

Properties of Tetrabrompyrocatechindibenzoate.—It crystallizes in transparent, square plates from a mixture of benzene and ligroin, and melts at 197° to a colorless liquid. It is soluble in benzene, or chloroform; slightly soluble in hot alcohol, methyl alcohol, or benzene; insoluble in ligroin.

If the tetrabrompyrocatechin was boiled gently with benzoyl chloride for only 5 or 10 minutes instead of several hours, a different product was obtained, which, after the usual purification, melted at 215° – 216° and, judging from a single analysis, was an impure monobenzoate of tetrabrompyrocatechin, as this would contain 60.36 per cent of bromine and we found 63.36 per cent. It crystallized from hot benzene in long, white needles. The substance was not of sufficient importance to make it worth while to prepare it in a state of purity.

Action of Hot Acetone.—One gram of tetrabromorthoquinone, dissolved in 1 gram of hot acetone, was heated for an hour on the steam-bath. The only solid product seemed to be the brilliant red hexabromorthoquinopyrocatechin ether. The vapor from the acetone was exceedingly irritating to the eyes and on adding water a heavy, dark colored oil, probably bromacetone, was precipitated.

Action of Acetophenone on Tetrabromorthoquinone.—In our experiments on the action of cold acetophenone on tetrabromorthoquinone we used either equal weights of the two substances or twice as much of the ketone as of the quinone. During the second and third days of standing red crystals of the quinone with acetophenone of crystallization¹ were deposited, but on longer standing they redissolved, and at the end of a week red and yellow crystals appeared, which, after a month, were followed by brown needles. These three products proved to be the same as those formed with acetone, that is $C_6Br_4O_2 \cdot C_6Br_2O_2$, $C_6Br_4O_2 \cdot C_6Br_2(OH)_2$ and $C_6Br_4(OH)O \cdot C_6Br_3O_2$, of which the last is formed in by far the largest quantity and, if the acetophenone is diluted with benzene, this seems to be the only aromatic product of the reaction, as was the case with acetone. After these products began to form the vapors from the solution became very irritating to the eyes, though not so much so as in the case of acetone, which is undoubtedly due to the slighter volatility of the acetophenone derivative. In order to determine the nature of this irritating substance, part of the filtrate from a mixture, which had deposited crystals of heptabromorthoquinopyrocatechin hemiether, was allowed to evaporate spontaneously; the residue consisted of crystals which melted, in the crude state, at 45° – 48° , whereas the ω -bromacetophenone melts at 50° . The rest of the filtrate was mixed with 4 volumes of aniline and 4 of alcohol and allowed to stand over night, when it deposited long, yellow needles which, after recrystallization from alcohol, melted at 94° (the melting point of ω -acetophenoneanilid is 93°). It follows, therefore, that the irritating substance was ω -bromacetophenone, $C_6H_5COCH_2Br$.

¹ Jackson and Porter: *THIS JOURNAL*, 31, 116 (1904).

When 1 gram of diethylketone was allowed to stand with 1 gram of the quinone, the red product appeared in 2 days, the yellow in 6, and the brown needles in 10. When the mixture was diluted with benzene, the yellow body alone was formed in 20 days. Mesityl oxide, with half its weight of the quinone, gave the red crystals with some of the yellow product in 6 days, and on longer standing a blackish brown mass. With benzene the yellow product was formed after 2 weeks.

Benzophenone, allowed to stand with its own weight of tetrabromorthoquinone, at 70° – 80° , gave no crystalline product even after 3 months, and the same negative result was obtained when the mixture was dissolved in benzene; when 1 gram of each was dissolved in five grams of chloroform, 0.5 gram of heptabromorthoquinopyrocatechin hemiether was obtained after 3 months. This result, however, we think was due to the action of the chloroform rather than to that of the benzophenone.

Action of Bromine and Acetone upon the Tetrabromorthoquinone.—The following experiments throw some light on the nature of the reaction. One gram of tetrabromorthoquinone mixed with 0.5 gram of acetone and 2 drops of bromine, after standing over night, was converted completely into the red and yellow products mixed with a little of the brown. A similar experiment without bromine (5 grams of quinone with 2.5 grams acetone) did not act for 24 hours, and the action was complete only in 60 hours, the product being principally the yellow compound.

A solution of 1 gram of the quinone in 5 grams of benzene, with 0.5 gram acetone and 3 drops of bromine, changed color in 1 night from red to straw-yellow, and left, on evaporation, crystals of the yellow product with white needles melting at 188° – 190° , which gave a yellow solution with sodic hydrate and a red product with nitric acid; they were, therefore, tetrabrompyrocatechin (melting point 187° , Stenhouse; 192° – 193° , Zincke). In the corresponding experiment without bromine, using 10 grams of benzene instead of 5 grams, the reaction did not begin until the mixture had stood 10 days, and was

complete in a fortnight, the product being the heptabromorthoquinopyrocatechin hemiether with no tetrabrompyrocatechin. It is evident, from these experiments, that the reactions run much more rapidly and further in presence of bromine than without it, which we ascribe to the reducing action of the hydrobromic acid formed in large quantity by the action of the bromine on the acetone.

Corresponding experiments with hexabromorthoquinopyrocatechin ether first made plain the properties of the dihydroxy compound formed from it by reduction, and thus enabled us to recognize as this body the blackish-brown product of the action of acetone on tetrabromorthoquinone. Two grams of the red hexabrom ether were mixed with 30 grams of acetone and 3 grams of bromine, and shaken until the reaction had taken place. If the shaking was omitted the ether collected in lumps, and the reagents then acted only superficially and, therefore, incompletely. After half an hour the red ether was converted entirely either into white, fibrous needles, or brown plates like mica, the yield in either case being 90 per cent of the red ether taken. In spite of many experiments we have not succeeded in determining the conditions which favored the formation of either of these products, except that the needles seemed to be more commonly formed when the proportion of acetone was large.

The two products, in spite of the difference in their appearance, proved to be identical. If recrystallized from alcohol, in which they are sparingly soluble, the white needles matting together like asbestos were obtained. If crystallized from nitrobenzene, each gave the brown plates like mica. Both decomposed at 306° – 307° , and gave the following results on analysis, in which I. was a specimen of the brown plates, and II. of the white needles, each recrystallized from nitrobenzene, and dried at 95° .

- I. 0.1537 gram of substance gave 0.2526 gram AgBr.
 II. 0.1226 gram substance gave 0.2006 gram AgBr.

Br	Calculated for $C_6Br_4O_2 \cdot C_6Br_2(OH)_2$	Found.	
		I.	II.
	69.56	69.93	69.63

For still greater certainty it was converted into the monobenzoyl ester by the action of benzoyl chloride.

0.1199 gram substance gave 0.1714 gram AgBr.

Br	Calculated for	Found.
	$C_6Br_4O_2 \cdot C_6Br_2(OH)OCOC_6H_5$.	
	60.45	60.82

Action of Aldehyds on Tetrabromorthoquinone.—Only two aldehyds were tried, oenanthol as a fat aldehyd and benzaldehyd to represent the aromatic series. As they gave essentially the same results as the ketones, we thought it not worth while to multiply experiments.

One gram of the quinone, after standing for 2 days with 2.5 grams of oenanthol, deposited red and yellow crystals of hexabromorthoquinopyrocatechin ether and heptabromorthoquinopyrocatechin hemiether, and after 6 days the whole of the quinone had been converted into these products. One gram of the quinone with 0.5 gram of oenanthol and 5 grams of benzene gave, after 20 days, the yellow product unmixed with any of the red.

One gram of the tetrabromorthoquinone stood with 2 grams of benzaldehyd. After 3 days the red color of the solution changed to straw-yellow, and the crystals of benzoic acid formed were colored yellow. After removing the benzoic acid with hot water, a mixture of the yellow and red products so often mentioned was obtained. The brown product was not obtained from either aldehyd, but probably would have been formed if the action had continued longer.

Octobromorthoquinhydrone, $C_6Br_4O_2 \cdot C_6Br_4(OH)_2 \cdot H_2O$. — This substance was prepared by Zincke,¹ but not analyzed or studied by him. He made it by mixing equal parts of tetrabrompyrocatechin and tetrabromorthoquinone, dissolved in benzene or ether. Our preliminary experiments showed that chloroform gave a better result than either of these solvents, as the product is so soluble in ether that it can be obtained only by evaporation, which is always accompanied by partial decomposition, while benzene converts it into heptabromorthoquinopyrocatechin hemiether so quickly that good results can be obtained

¹ Ber. d. chem. Ges., 20, 1778 (1887).

only by very rapid work. Chloroform, on the other hand, gave the substance in a pure state, without difficulty, by the following process: Equal parts of tetrabromorthoquinone and tetrabrompyrocatechin were dissolved, separately, in the least possible quantity of hot chloroform, the solutions mixed and immediately cooled, when long black crystals were deposited, which, after pressing between filter paper, were dried *in vacuo* for analysis. Analyses I., II., III. and IV. That the solvent did not influence the nature of the product is shown by Analyses V., and VI. which were made with specimens prepared from hot benzene, to which its own volume of ligroin had been added before cooling.

I. 0.6553 gram of substance gave 0.3982 gram CO_2 and 0.0454 gram H_2O .

II. 0.3194 gram substance gave 0.5560 gram AgBr.

III. 0.1817 gram gave 0.3161 gram AgBr.

IV. 0.2405 gram gave 0.4183 gram AgBr.

V. 0.2410 gram gave 0.4169 gram AgBr.

VI. 0.2736 gram gave 0.4737 gram AgBr.

	Calculated for $\text{C}_{12}\text{Br}_8\text{O}_4\text{H}_2 \cdot \text{H}_2\text{O}$.	I.	II.	Found. III.	IV.	V.	VI.
C	16.60	16.58
H	0.46	0.78
Br	73.70	. .	74.08	74.04	74.03	73.62	73.69

The substance, therefore, is not the expected quinhydrone which requires 16.94 C, and 75.40 Br, but this substance combined with 1 molecule of water. We were led to this conclusion by the following considerations: The anomalous results given above were not caused by impurities in the tetrabromorthoquinone or tetrabrompyrocatechin used, since analyses of these compounds showed they were pure. The low result on the bromine was not due to a loss of hydrobromic acid, or bromine, since we passed air for 15 minutes through a boiling benzene solution of equal parts of tetrabromorthoquinone and tetrabrompyrocatechin, during which time the air gave no reaction with moist litmus paper and no precipitate with a solution of argentic nitrate, whereas, in the formation of the quinhydrone, the solutions were not boiling for more than 1 minute.

If the experiment described above was continued for more than 15 minutes hydrobromic acid was given off, but its evolution was accompanied by the formation of heptabrompyrocatechin hemiether. As there was no loss of bromine or hydrobromic acid in the formation of the quinhydrone, the low results in the analyses must be due to the addition of some substance, and as the same product was obtained from chloroform and benzene solutions, this substance must be water. Such an addition of water is not without analogy, as Porter and one of us¹ obtained a water compound, $(C_6Br_4O_2)_2 \cdot H_2O$, by the action of ordinary benzene or toluene on tetrabromorthoquinone.

In the hope that a mixture of chloroform and an alcohol might cause the addition of the alcohol instead of water, a new specimen of the quinhydrone was made with a washed sample of chloroform, dried over calcic chloride and then mixed with 5 per cent of isoamyl alcohol. This gave the following result:

0.3142 gram substance gave 0.5469 gram AgBr.

	Calculated for $C_{12}Br_8O_4H_2 \cdot H_2O$.	Found.
Br	73.70	74.08

This specimen, therefore, has also taken up water and we can infer from this experiment that the quinhydrone has little or no tendency to combine with alcohols.

The analytical results given above cannot show in what proportion the two constituents exist in the quinhydrone; this was done, therefore, by the following synthetic experiments:

1. Two grams of tetrabromorthoquinone and 2 grams of tetrabrompyrocatechin were dissolved in 10 grams of hot chloroform, mixed and cooled. Nearly 2 grams of the black quinhydrone crystals were deposited and the mother liquor, when evaporated by a stream of dry air, gave only black crystals with no sign of either of the components.

2. Two grams of the quinone and 1 gram of the pyrocatechin, treated in the same way, gave 1 gram of black quinhydrone crystals and the mother liquor, on evaporation, showed that an excess of the quinone was present.

3. Two grams of the quinone with 4 grams of the pyro-

¹ THIS JOURNAL, 31, 109 (1904).

catechin gave 3 grams of quinhydrone crystals and the mother liquor contained an excess of the pyrocatechin.

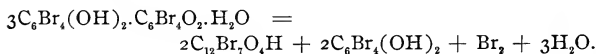
These experiments show that 1 molecule of the tetrabromopyrocatechin combines with 1 molecule of the tetrabromorthoquinone to form the quinhydrone, which, therefore, has the formula $C_6Br_4O_2 \cdot C_6Br_4O_2 \cdot H_2 \cdot H_2O$ assigned to it earlier.

Properties of the Octobromorthoquinhydrone.—It is deposited from its hot solution in chloroform in shining black needles, or slender prisms, sharply pointed at one end and often more than 1 cm. long. When heated to 110° it turns brown without melting, and it was found that this change of color was attended with a loss in weight.

1.4877 grams substance, heated to 110° for 6 hours, lost 0.1050 gram.

	Calculated.	Found.
Br + H ₂ O	8.22	7.05

The brownish red residue, on crystallization from benzene, was found to contain heptabromorthoquinopyrocatechin hemiether, $C_6Br_4(OH)O \cdot C_6Br_3O_2$, and tetrabrompyrocatechin. The most probable reaction for the formation of these two substances would be

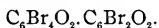


The loss of $Br_2 + H_2O$ calculated for this reaction is given under the head "calculated" above, and agrees perhaps as well as could be expected with the amount found.

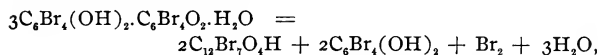
The quinhydrone is freely soluble in ether; soluble in cold chloroform, more soluble in hot; rather more soluble in benzene than in chloroform; slightly soluble in ligroin; insoluble in water. Of all these solvents chloroform is the best, as the substance can be recrystallized from it, if the work is carried on quickly enough, although by long standing with chloroform the quinhydrone is converted into heptabromorthoquinopyrocatechin hemiether and tetrabrompyrocatechin. This change takes place much more rapidly in benzene solution, so that it is hard to get crystals of quinhydrone, free from these

impurities, when benzene is used in its preparation. Cold benzene brings about the change in 2 or 3 weeks, but with boiling benzene it was found to be complete in 3 hours.

To study this reaction more carefully 2 grams of tetrabromorthoquinone and 2 grams of tetrabrompyrocatechin were boiled for 5 hours, with 10 grams of benzene, when, on evaporating off the solvent, good crystals of the hemiether and of tetrabrompyrocatechin were obtained. To determine the amount of each the residue was boiled with dilute alcohol for 1 hour, which converted the hemiether completely into the insoluble hexabromorthoquinopyrocatechin ether,



This was filtered out and found to weigh 2 grams; and upon adding water to the filtrate, 1.5 grams of tetrabrompyrocatechin were obtained. The reaction given earlier,



followed by the conversion of the hemiether into the complete ether, $\text{C}_6\text{Br}_4\text{O}_2 \cdot \text{C}_6\text{Br}_2\text{O}_2$, requires 2.11 grams of this from 4 grams of the quinhydrone and 1.31 grams of tetrabrompyrocatechin: our numbers (2 grams and 1.5 grams) are as near as we could expect with the rough methods of determination used.

When hot alcohol is used as a solvent for the quinhydrone, the decomposition goes to the formation of the red hexabrom ether mentioned above. If the quinhydrone was allowed to stand with alcohol in the cold, small red needles were obtained, probably the compound $(\text{C}_6\text{Br}_4\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{OH}$, colored red by the hexabrom ether. Methyl alcohol, propyl alcohol, or isopropyl alcohol gave yellow or white crystals under these conditions, which were not examined, as they were supposed to be impure specimens of the corresponding α -bodies.

The quinhydrone was not reduced by aqueous sulphurous acid, probably on account of its insolubility in water, but by passing sulphurous dioxide into a solution of it in ordinary benzene, tetrabrompyrocatechin was obtained. When the

quinhydrone was boiled for 15 minutes with acetic anhydride, the deep red color of the solution gradually turned to light yellow and the product, after boiling with water and recrystallization from benzene, showed the constant melting point 214° and was, therefore, the diacetate of tetrabromopyrocatechin.

Tetrabromopyrocatechin Diacetate, $C_6Br_4O_2(C_2H_3O)_2$.—This substance was made as follows, for comparison with products from other reactions: Five grams of tetrabromopyrocatechin were boiled for 1 hour, with 15 grams of acetic anhydride. On cooling, large colorless plates were deposited, which were purified by recrystallization from benzene till they showed the constant melting point 215° – 216° , when they were dried at 95° for analysis:

0.2711 gram substance gave 0.4024 gram AgBr.

	Calculated for $C_6Br_4(OC_2H_3O)_2$.	Found.
Br	62.73	63.18

Properties.—It crystallizes from benzene in colorless, square plates, which melt at 215° – 216° to a colorless liquid. It is soluble in chloroform whether cold or hot; slightly soluble in alcohol, benzene, or ether when cold, soluble in these solvents when hot; essentially insoluble in water or ligroin.

Tetrabromorthoquinone and Organic Acids.—In taking up this puzzling subject we tried first to obtain from the action of warm acetic acid on tetrabromorthoquinone Koch's¹ white product, $C_{14}H_2Br_8O_6$, which melts at 230° to a colorless liquid, a fact which we confirmed with a specimen left from his research. Porter,² who repeated Koch's process as nearly as possible, obtained yellowish white, efflorescent, rectangular plates or prisms, melting to a red liquid, at 220° – 230° , and containing over 2 per cent less bromine. In addition to many unsuccessful preliminary experiments, we tried two on a large scale in which the utmost care was taken to have the conditions the same as those used by Koch, but in each case the whole white crude product was converted into the red hexabromorthoquinopyrocatechin ether during the crystallization.

¹ THIS JOURNAL, 26, 42 (1901).

² *Ibid.*, 31, 114 (1904).

Accordingly, in a third experiment, we changed the method of purification, which consisted, according to Koch, in extracting the crude product with 200 cc. of hot alcohol, filtering hot, and, after it had cooled, filtering again; then the filtrate was diluted with 200 cc. of water, and the white precipitate recrystallized from glacial acetic acid, until it showed the constant melting point 230° . We now recrystallized the white precipitate, thrown down by water, from benzene instead of acetic acid, and obtained long, yellow needles which decomposed, with reddening, at 235° – 250° , Analysis I. In a fourth experiment the crude product was purified only by crystallization from benzene, without the use of alcohol or acetic acid. The substance obtained in this way also crystallized in long, yellow needles, and decomposed, with reddening, at 235° – 250° . Analysis II.

I. 0.2430 gram substance gave 0.4202 gram AgBr.

II. 0.1806 gram substance gave 0.3102 gram AgBr.

	I.	Found.	II.
Br	73.58		73.11

These results show that the two products are the same, but different from that of Koch (71.45 per cent Br) or of Porter (69.26 per cent Br). The nature of our compound will be discussed later, after we have described other ways in which it was obtained.

The following experiments, in which the conditions of the reaction were somewhat varied, gave different results. Ten grams of tetrabromorthoquinone were dissolved in 20 grams of acetic acid, and heated in an Erlenmeyer flask, on the steam-bath, until all the acid had evaporated; the product was essentially pure heptabromorthoquinopyrocatechin hemiether, which was produced by the longer action of the warm acetic acid during its evaporation from the Erlenmeyer flask instead of the evaporating dish used in the earlier experiments. Five grams of the quinone were boiled, for 7 hours, with 15 grams of acetic acid; the solution, on evaporation, yielded a yellow mass containing white needles of tetrabrompyrocatechin. The more complete reduction in this case was evidently due to

the higher temperature at which the reaction took place, 118° instead of 100° .

We also studied the action of cold acetic acid on tetrabrom-orthoquinone. Ten grams of it were allowed to stand in a corked flask, at ordinary temperature, with 20 grams of glacial acetic acid. In 2 weeks thick prisms had formed, some of which were yellow, others red, but we do not think these were the two products of Porter,¹ as the yellow prisms were evidently the final product about to be described, and the red looked like tetrabromorthoquinone crystallized from acetic acid. After standing for 2 months only one substance remained which crystallized in well characterized, light yellow, thick prisms or rhombic plates. We have repeated this experiment 12 times, and in each case obtained this product and no other. Some of it was recrystallized from glacial acetic acid, and dried at about 50° for analysis, during which drying it lost no weight.

I. 0.3466 gram of substance gave 0.2716 gram CO_2 and 0.0426 gram H_2O .

II. 0.2491 gram of substance gave 0.3583 gram AgBr.

III. 0.2915 gram of substance gave 0.4198 gram AgBr.

	Calculated for ($\text{C}_6\text{Br}_4\text{O}_2$) ₂ ·($\text{C}_2\text{H}_4\text{O}_2$) ₃ .	I.	Found. II.	III.
C	21.02	21.37
H	1.17	1.37
Br	62.24	. .	61.22	61.30

The results agree better with the formula given than with any other we could find. As it did not melt, we had no criterion of purity for it, but the large homogeneous crystals indicate that it was not very impure, and the fact that we obtained it from 12 different preparations is good evidence that it is a definite compound. Many attempts were made to determine the amount of acetic acid contained in the substance by titration with a sodic hydrate solution, but no constant results were obtained in water, alcohol or benzene. The numbers varied between 19 and 24 per cent, whereas the formula given above requires 17.51 per cent.

¹ See the introduction.

Properties.—The addition compound of tetrabromorthoquinone and acetic acid crystallizes in nearly square, white, rhombic plates from glacial acetic acid. As obtained at first it frequently forms thick, square prisms of a pale yellow color. It does not melt under 300° , but gradually turns red when heated, although stable at 50° . It is soluble in alcohol, ether, benzene, or chloroform; very slightly soluble in cold acetic acid, moderately soluble in it when hot; insoluble in water, or ligroin. Strong nitric acid does not act on it. Sodid hydrate, in aqueous solution, turns it white, but does not dissolve it. As stated already, part of the sodid hydrate is neutralized by the action of this body upon it. As we thought it might be an α -body, we tried the various methods for converting an α - into a β -body, but boiling with acetic acid, heating with acetic anhydride and sodic acetate, or boiling with dilute sodid hydrate brought about no such conversion.

Crystallization from benzene decomposed the addition compound $(C_6Br_4O_2)_2 \cdot (C_2H_4O_2)_3$ as shown by the following bromine determinations: The original substance, 61.30 per cent; after 1 crystallization, 70.52 per cent; after 4, 71.73 per cent; after 10 crystallizations, 73.16 per cent. This final product is evidently identical with the substances obtained by the action of warm acetic acid followed by crystallization from benzene, which contained 73.58 and 73.11 per cent of bromine, since all of them consist of long, yellow needles, decomposing at 235° – 250° . It gave the following results on analysis, but there is some doubt whether the specimen analyzed for C and H had been recrystallized as often as that used for Br.

I. 0.3088 gram substance gave 0.2194 gram CO_2 and 0.0137 gram H_2O .

II. 0.2872 gram substance gave 0.4937 gram AgBr.

	I.	Found.	II.
C	19.37		.
H	0.50		.
Br	.		73.16

As the same compound was obtained with formic acid, the

discussion of its formula is given after all the analytical data have been presented.

Action of Other Organic Acids with Tetrabromorthoquinone.—If the quinone was warmed with formic acid, in an Erlenmeyer flask, on the steam-bath, in about 15 minutes it was converted into heptabromorthoquinopyrocatechin hemiether.

Two grams of the quinone, mixed with 10 grams of formic acid, were allowed to stand, at ordinary temperatures, in a corked flask. In 4 days yellow crystals were deposited from the red solution; in 10 days the solution itself had turned yellow. The product was recrystallized 3 times from benzene, which did not alter its decomposition point, 232° – 234° . In appearance and properties it resembled the products obtained from acetic acid after crystallization from benzene, and the analyses showed they were the same.

I. 0.2545 gram substance gave 0.1783 gram CO_2 and 0.0110 gram H_2O .

II. 0.2716 gram substance gave 0.4717 gram AgBr.

III. 0.3186 gram substance gave 0.5525 gram AgBr.

	I.	Found. II.	III.
C	19.11	.	.
H	0.48	.	.
Br	.	73.91	73.81

Analysis II. was made with a specimen from a different preparation from that used for I. and III. As this substance has been obtained also by 3 somewhat different methods with acetic acid, there can be little doubt that it is a definite compound. Its percentage composition agrees well with that for the ether or oxide corresponding to the heptabromorthoquinopyrocatechin hemiether.

	Calculated for ($\text{C}_6\text{Br}_4\text{O} \cdot \text{C}_6\text{Br}_3\text{O}_2$) $_2\text{O}$.	Formic acid.	Found.	Acetic acid.
C	18.95	19.11	19.37	
H	0.00	0.48	0.50	
Br	73.69	73.81	73.91	73.16 73.58 73.11

It may, therefore, be called diheptabromorthoquinopyrocatechin ether, but more experimental work is necessary be-

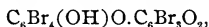
fore this formula can be considered definitely established. The only confirmatory work done by us consisted in recrystallizing a specimen, made with acetic acid, from benzene 12 times, when it seemed to be partially converted into the heptabrom-orthoquinopyrocatechin hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, a result in harmony with the formula proposed above.

Properties of Diheptabromorthoquinopyrocatechin Ether.—It crystallizes from benzene in long, yellow needles, which turn white on long exposure to the air, but this change is not associated with any change in the decomposition point. If recrystallized from benzene, the white crystals become yellow again. When heated very rapidly from temperatures above 200° it melts, with reddening, between 235° – 250° ; 232° – 234° was the most definite temperature observed, but, if heated slowly, it turns red without melting. Its solution in ether or alcohol yields white crystals, although alcohol sometimes converts it into a brilliant red substance, probably the hexabromorthoquinopyrocatechin ether; a solution in benzene or carbonic disulphide gives yellow needles. Aqueous sodic hydrate darkens it.

Propionic acid, butyric acid, or isovalerianic acid gave, with the quinone in the cold, yellow crystals, apparently the same as those obtained from formic acid, but the following analyses, made after crystallization from benzene, indicate that these products, if the same, are somewhat impure:

	Butyric acid.	Isovalerianic acid.	
C	20.03	20.88	20.47
H	0.42	0.37	0.63
Br	72.36	72.36	. .

Five grams of the quinone, heated on the steam-bath with 10 grams of propionic acid, after 2 days became yellowish red, and deposited a mixture of the heptabrom hemiether,



and unaltered tetrabromorthoquinone.

Action of Bromine and Nitric Acid on Tetrabromorthoquinone.—The experiments described in this section were undertaken in the hope of making an addition compound of tetrabrom-

orthoquinone with bromine similar to those obtained from paraquinones by Nef,¹ and we had good hope of success because Zincke and Küster² have made a hexachlororthobenzoquinone, but none of our experiments gave any indication of the formation of such a compound. Bromine, in chloroform solution, had no action, even when boiled for 7 hours, or exposed to sunlight 6 days.

In one experiment, to be sure, the quinone with chloroform and bromine, heated to 100°, in a sealed tube, 4 hours, gave a new substance, which, however, seemed to be the yellow product described later and, therefore, not a bromide.

When tetrabromorthoquinone was heated with a mixture of fuming nitric acid and bromine, 2 new compounds were formed. The following conditions gave good results: Ten grams of tetrabromorthoquinone were mixed with 50 cc. of fuming nitric acid and 5 cc. of bromine and the mixture heated in an Erlenmeyer flask, on the steam-bath, until the bromine had volatilized. On cooling, large yellow plates of the first compound separated, which were recrystallized from a mixture of 1 part of benzene and 1 of ligroin, until they showed the constant melting point, 142°. If the heating was continued longer another compound was formed, which was white and soluble in water and could, therefore, be easily separated from the insoluble, yellow product by washing. The same substances were obtained by the action of fuming nitric acid alone on the tetrabromorthoquinone, the necessary bromine being furnished by the decomposition of part of the quinone, but the yield in this case was even smaller than when nitric acid and bromine were used. In any case the yield left much to be desired, as most of the quinone was oxidized completely, and too long boiling destroyed both of the products.

The Yellow Product.—The substance, purified as described above, was dried at 100° for analysis:

I. 0.3286 gram substance gave 0.1828 gram CO₂ and 0.0104 gram H₂O.

¹ J. prakt. Chem., [2], 42, 182 (1890).

² Ber. d. chem. Ges., 22, 486 (1889).

II. 0.3232 gram substance gave 0.1710 gram CO_2 and 0.0055 gram H_2O .

III. 0.2043 gram substance gave 0.3729 gram AgBr.

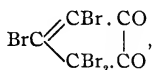
IV. 0.2761 gram substance gave 0.5041 gram AgBr.

	Calculated for $\text{C}_5\text{Br}_4\text{O}_2$	I.	II.	Found. III.	IV.
C	14.57	15.17	14.43
H	0.00	0.35	0.19
Br	77.67	77.67	77.69

The substance, therefore, is probably the tetrabromcyclopenteneorthoquinone, and we have adopted this constitution, provisionally, for it, as in harmony with all our observations, but, unfortunately, it was discovered so late in the year that we are unable to furnish a certain proof of its structure.

Properties of the Tetrabromcyclopenteneorthoquinone—It crystallizes from fuming nitric acid in thick plates, from a mixture of benzene and ligroin in large prisms which are, apparently, monoclinic. Its color is a full yellow, like that of potassic chromate. It melts at 142° with no signs of decomposition, and is soluble in alcohol, ether, chloroform, benzene, or acetone; slightly soluble in ligroin; insoluble in water. An aqueous solution of sodic hydrate has no effect on it in the cold, but if warmed decomposes the compound with formation of hypobromous acid, to judge by the smell. Sodic alcoholate converts it into a red substance even in the cold.

The compound was supposed to be the tetrabromcyclopenteneorthoquinone,



for the following reasons: With orthophenylenediamine it gave a brown, amorphous compound, which we could not succeed in crystallizing, so it was not analyzed, but with cold sulphuric acid it gave the dark red color characteristic of diphenylenequinoxaline. When it was boiled for an hour with an equivalent amount of 3,5-dibrom-1,2-phenylenediamine and 20 times its weight of alcohol, the dark solution deposited

small, colorless needles in moderate amount, which were dissolved in absolute alcohol, precipitated with water and crystallized once from absolute alcohol. The dark colored crystals were barely enough for analysis.

0.0644 gram substance gave 0.0963 gram AgBr.

	Calculated for $C_5Br_2(N_2C_6H_2Br_2)_2$.	Found.
Br	64.51	63.63

Little weight can be given to this analysis, owing to the small amount of substance used and the fact that there was no criterion of purity, as it blackened, without melting, at 308° . On the other hand, the fact that this substance also gave a red color with strong sulphuric acid tells in favor of the formula ascribed to it above. The yellow substance oxidized dimethylaniline in the cold, which also would indicate that it is a quinone. We hope that the study of the substance in this laboratory during the next academic year will determine its constitution with certainty.

The White Product of the Action of Nitric Acid and Bromine on Tetrabromorthoquinone.—This substance was formed by the longer action of the reagents, but we are not yet clear whether it is produced from the yellow body or at the same time with it. The compound crystallizes in white needles, which melt at 144° – 146° , are very soluble in water, and give an acid reaction. It was discovered so late in the year that we were unable to study it properly, so that several analyses of the acid and its silver salt gave discordant results, showing that the substances had not been thoroughly purified. At first sight it showed some resemblance to dibrommalonic acid, which melts at 147° , with evolution of carbonic dioxide¹, and is converted into dibromacetic acid by heating it with water to 50° – 60° ; our compound melted at 144° – 146° with partial decomposition, and gave off carbonic dioxide, when boiled with water, but the aniline salt of our acid melted at 150° – 152° , whereas the dibrommalonate of aniline melts at 113° . The facts collected so far, by us, therefore, indicate that the acid is a new com-

¹ Conrad and Reinbach: Ber. d. chem. Ges., **35**, 1817 (1902). Willstätter: *Ibid.*, **35**, 1376 (1902).

zinc electrodes remain intact even in ethyl alcohol. Svedberg then applied Bredig's method to organic solvents, but found that the solvent decomposed, with separation of carbon and other undesirable reactions, if the current was strong enough to cause cathode diffusion of the metal.

Finally, he succeeded in working out two methods. In the first the metal, in the form of sheets of thin foil, is suspended in the solvent; the electrodes are of metals not easily diffused, such as iron and aluminium; the difference of potential is 110 volts. With an intense development of sparks on the very large surface of the foil, the metal diffuses, while the current is so small that it can scarcely be measured by an ammeter. This is the essential of both of Svedberg's methods: high voltage, very low current. By this method he has obtained organosols of tin, gold, silver and lead in different solvents. The method fails, however, with metals like aluminium and iron, which resist cathode diffusion. With aluminium foil he obtained spark phenomena but no colloid.

His second method was devised to overcome this difficulty, by using a still higher potential, while keeping the current low to avoid decomposition of the solvent. Using an induction coil of 12 cm. spark length, he put in a glass condenser of 225 cm.² surface, parallel to the secondary of the coil, and led the secondary poles to electrodes which dipped into the solvent in a porcelain dish. The metal was used either in granular form or in pieces of wire. On closing the circuit there is a vigorous sparking between the metal particles, the solvent at once darkens and, in a few minutes, a dark colored organosol is formed. It is, of course, better to use electrodes of the metal which is reacting, but he finds, experimentally, that the influence of the electrodes is very slight. By this method Svedberg has prepared a series of new colloids, comprising magnesium, zinc, aluminium, tin, antimony, iron, nickel, sodium and potassium.

While hydrosols of copper, copper-zinc, silver, gold, lead and bismuth have been made by previous observers, these organosols, excepting silver, are new; of those mentioned above, the copper and bismuth organosols were made by the second method, the others by the first one.

The organosols of sodium and potassium are very unstable; but the author has experimental ground for hoping to obtain more stable organosols of these metals.

It is of interest that the sodium organosols in ligroin, ligroin-naphthalene and ether are violet in color, while the corresponding potassium organosols are bluish violet. It is

known that cathode rays or Tesla currents act on the chlorides of sodium and potassium, turning them blue. Wiedemann¹ thinks that the blue color is caused by the formation of subchlorides. Elster and Geitel, however, believe the blue color to be due to solid colloidal solutions of the metals in their chlorides. The observed colors of the organosols would support the view of Elster and Geitel.

Svedberg considers this work preliminary and reserves the field.

E. RENOUF.

The Stereoisomerism of Substituted Ammonium Compounds.

The preparation of stereoisomeric nitrogen derivatives has engaged the attention of a number of chemists during the past few years, and although, on the experimental side, a considerable degree of success has attended their labors, the theory of the subject has not, hitherto, been in a satisfactory state. An exception must be made in favor of the "syn" or "anti" compounds, of the type $RR'C:NR''$, such as unsymmetrical oximes, which are beyond the scope of this report.

The difficulties referred to arise from the fact that a few cases of isomeric compounds of the type $NR_3R'X$ ($X = \text{halogen}$) have been described, but no isomerides of the type $NR_1R'R''X$ could be prepared, except in the case of dicycloid compounds containing a nitrogen atom in each ring. The first example of this was observed by Aschan, it is doubtless due to the absence of free rotation. Compounds of the type $NR_1R'R''R'''X$ have been repeatedly shown to exist in optically active forms and Wedekind² has examined a large number of such substances to determine the existence of spatial isomerides but, with the sole exception of the phenylbenzylmethylallylammonium salts, which he himself prepared,³ all the derivatives of this type which previously had been regarded as stereoisomeric were found to differ in structure.

His conclusions in regard to phenylbenzylmethylallylammonium salts were confirmed, later, by Hantzsch and Horn.⁴

Some little time ago Le Bel showed⁵ that the difference between compounds of the type $NR_3R'X$, which he had believed to be due to isomerism, in fact arose from isomorphism.

Kipping⁶ proved that the salts of optically active acids and hydrindamine, which he had previously described, were not isomerides of the base, but were salts of isomeric acids. Hence,

¹ Wiedemann Ann., 64, 78.

² Ber. d. chem. Ges., 36, 178 (1902); 38, 436 (1905).

³ Ibid., 32, 517, 3561 (1899).

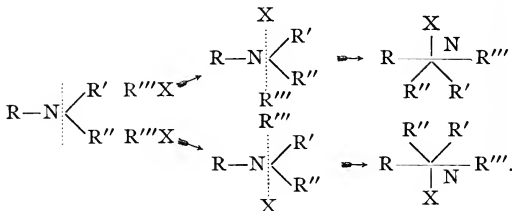
⁴ Ibid., 35, 883 (1902).

⁵ J. Chim. Phys., 2, 340 (1904).

⁶ J. Chem. Soc., 87, 628 (1905).

it follows that no instance of spatial isomerism in an ammonium derivative has ever been observed except Wedekind's compound referred to above. In a recent paper¹ H. O. Jones records the results he has obtained by a reexamination of Wedekind's isomers. Neither compound can be transformed into the other. Unlike the β -compound the α -derivative is unsaturated, as is shown by the potassium permanganate test. The substances differ in other ways, including their action on methyl iodide, and on analysis it was found that the β -compound is really phenylbenzyltrimethylammonium iodide, $C_6H_5N(CH_3)_2CH_2C_6H_5I$, while the α -derivative is the true phenylbenzylmethylallylammonium iodide, $C_6H_5NCH_3(CH_2C_6H_5)CH:CHCH_3I$. Thus the last instance of stereoisomeric ammonium derivatives is shown to be without existence in fact.

In the light of these observations Jones discusses the various suggestions which have been offered by Werner, van't Hoff, Willgerodt, Wedekind and Bischoff regarding the configuration of the ammonium derivatives, deciding in favor of Bischoff's "pyramidal" formula, with some simplification suggested by himself. He represents the formation of an ammonium salt from an amine, graphically, as follows:



The intermediate substance is regarded as being "a very unstable compound or as possibly only a state which arises when the amine and alkyl iodide first come within the sphere of each other's action." R''' and X must be able to take up either of the two available valencies, because equal portions of *d*- and *l*-isomerides are always produced. The three groups in trivalent nitrogen compounds lie in the same plane as the nitrogen atom, during the change of valency the radicles group themselves into the most stable configuration, which is always the same for the same five radicles and is independent of the order in which they are introduced into the molecule. The author

¹ J. Chem. Soc., 87, 1721 (1905).

has written a highly interesting paper, and has materially contributed to the simplification of a troublesome and somewhat difficult subject.

J. BISHOP TINGLE.

REVIEWS.

HYPOCHLORITE UND ELECTRISCHE BLEICHE—Theoretischer Theil. By DR. EMIL ABEL. Monographien über angewandte Electrochemie. Band XVII. Halle a. S.: Wilhelm Knapp. 1905. pp. 110. Price, M. 4.50.

Although almost a century has elapsed since Cruikshank first prepared sodium hypochlorite by the direct electrolysis of brine, the practical application of the idea has, for various reasons, never become an important factor in the bleaching industry. The reactions which obtain when an electric current is passed through a solution of common salt were found to be much more complicated than were formerly supposed, and, owing to the experimental difficulties involved in their study, the theory of the process has, until very recently, been little considered.

A very complete description of the various forms of apparatus which have been developed for the commercial production of bleaching liquor by direct electrolysis, appeared as Volume VIII of the series of monographs of which this work forms a part. Under the title, "Theorie der Hypochlorite," the author, some time ago, published a brochure in which he treated the subject at length, from a chemical point of view. In the present volume he has developed the process from the energy standpoint, giving the matter a purely thermodynamical treatment. He finds that, in this way, not only can the function of the electric current in the formation of hypochlorites be most easily determined, but that by thermodynamics alone can the true energy efficiency of the different technical methods for the preparation of hypochlorites be obtained.

The first part of the monograph is devoted to the calculation of the critical voltages of all the ions concerned in the reactions. A table giving the theoretical electromotive force necessary for the liberation of each ion of the first product is given.

The mechanism of the reactions taking place to form hypochlorite and also chlorate is discussed at length, the author giving great weight to the work of Foerster and his students on the theory of chlorate formation.

Those interested in the practical application of electrolysis for the production of bleaching liquor will find, however, the

last portion of the work of greater value than the first two-thirds, based as they are, on assumptions which, for the most part, are impossible of realization. In discussing the condition which must be observed in order that the maximum energy efficiency may be obtained, and the effect of the various additions to the brine which have from time to time been proposed, the author has rendered a distinct service to the electrochemist and engineer.

W. H. W.

VERFLÜSSIGTES AMMONIAK ALS LÖSUNGSMITTEL. Materialien über die chemischen Eigenschaften des verflüssigten Ammoniakgases. Gesammelt von J. BRONN. Berlin: Julius Springer, 1905. pp. 251. Price, M. 6.

During the last forty years much work on liquid ammonia has been published, which Herr Bronn has collected and classified in this volume. While the author is especially interested in the technical uses of liquid ammonia as a solvent, the book will be of value to chemists generally. To indicate its scope, there are chapters on the properties of liquid ammonia; on the action of gaseous ammonia as a liquefier, with special reference to the work of Divers; on the absorption of ammonia by different substances; on liquid ammonia as a solvent; on metalammonium compounds and metalamids; on reactions and syntheses in ammonia solution; on reactions of the metalamids; and on physical-chemical work on liquid ammonia.

E. R.

A TEXT-BOOK OF PHYSIOLOGICAL CHEMISTRY FOR STUDENTS OF MEDICINE. BY JOHN H. LONG, M.S., Sc.D., Professor of Chemistry in The Northwestern University Medical School, Chicago. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1905. pp. 424. Price, \$2.50 net.

The writer has here presented a good elementary text-book of physiological chemistry for medical students. The style is clear and concise. The subject matter is divided into four sections as follows: The Nutritives; Ferments and Digestive Processes; The Chemistry of the Blood, the Tissues and Secretions of the Body; The End Products of Metabolism, Excretions, Energy Balance.

The directions for many experiments are inserted in the body of the text in fine print, so that the book will also serve as a laboratory manual for a brief course. Much of the recent work, such as Fischer's polypeptide investigations, is briefly presented by the author, and he also discusses in detail the tests of value to clinical medicine, such as the examination of stomach contents, faeces, etc., in consequence of which the pure physiological chemistry suffers considerable abridgment. A few inaccuracies of very minor importance have been noted.

Thus on p. 313 the statement is made that amyl salicylate is very readily hydrolyzed by liver extract whereas, compared with other esters, this one is really hydrolyzed by it very slowly indeed. On the whole the book is satisfactory and deserves to be recommended.

A. S. L.

ELEKTROMAGNETISCHE SCHWINGUNGEN UND WELLEN. VON DR. JOSEF RITTER VON GEITLER. Braunschweig: Friedrich Vieweg und Sohn. 1905. Price, M. 4.50.

This volume on the subject of "Electro-Magnetic Vibrations and Waves" will not be of much interest to a student of chemistry, inasmuch as, up to this time, they have very few applications to chemical phenomena. To the physicist, however, the book is one of importance, and any one interested in the historical development of the subject will find it most profitable. The mathematical treatment is simple yet explicit; the description of experiments is clear and up to date, the references, specially to modern work, are most complete and the text is written in a lucid and attractive manner. Taken from every standpoint, therefore, the book is one to be recommended to all students of Philosophy, however advanced.

J. S. A.

ANNUAL REPORTS OF THE PROGRESS OF CHEMISTRY FOR 1904. Issued by The Chemical Society. Vol. I. London: Guernsey & Jackson. New York: D. Van Nostrand Co. 1905. Price, \$2.00 net.

In this volume the English Chemical Society begins a series of annual reports on the progress of chemistry. The book covers the same field as Meyer's "Jahrbuch der Chemie" which has been published yearly since 1891. The "Jahrbuch" for 1903 contains 600 pages, the volume reviewed contains 280 pages. This is a distinct gain for the English journal, as such reports should be as brief in detail as possible. The table of contents shows that the different chapters are in competent hands: Chemistry, general and physical, James Walker; Inorganic, P. P. Bedson; Organic-aliphatic, H. J. H. Fenton; Organic-aromatic, J. B. Cohen; Stereo, W. J. Pope; Physiological, W. D. Halliburton; Agricultural, J. A. Voelcker; Mineralogical, A. Hutchinson; and Radioactivity, F. Soddy.

E. R.

METHODS OF ORGANIC ANALYSIS. By HENRY C. SHERMAN, PH.D. New York: The Macmillan Company. 1905. Price, \$1.75.

The purpose of this little work is to furnish students of organic chemistry with a convenient handbook for conducting the most common operations which they will be called upon to perform in the analysis of ordinary commercial products.

Chapter I. treats of the principles of ultimate and proximate

analysis. In the second chapter are given the standard methods for the determination of nitrogen, sulphur and phosphorus. The third chapter, on alcohols, is one of special interest at the present time, when chemists throughout the world are devoting so much attention to the analytical methods applied to beverages. The methods described mention all the prominent processes in the light of recent experience. The oxidation method for alcohols, comprising the substance known as fusel oil, has practically taken the place of Rouse's old process. The oxidation method gives fairly satisfactory results when applied to known quantities of the fusel oils. The statement by the author, therefore, that "neither method gives very satisfactory results" should be modified as applying only to the volumetric method. It has been found, also, that carbon tetrachloride is a better solvent for the fusel oils than chloroform. The author fails to mention this fact. The colorimetric method of determining the fusel oils is not referred to.

Chapter IV. deals with aldehydes; Chapter V. with the general methods for the carbohydrates; Chapters VI. and VII. with special methods. Chapter VIII. is devoted to the organic acids, especially to those of the aliphatic series. Chapter IX. treats of the general methods of examining oils, fats and waxes, and Chapter X. of the special methods for fatty oils. The salad oils are particularly mentioned in this chapter. Chapter XI. is devoted to butter; Chapter XII. to soaps and lubricants; Chapter XIII. to the proteids and cereals; and Chapter XIV. to milk. In the latter special attention is given to the preservatives which are used therein.

This book will prove useful to students and analysts in their work with foods and food products.

H. W. W.

AMERICAN CHEMICAL JOURNAL

VISCOSITY AND FLUIDITY.¹

BY EUGENE C. BINGHAM.

PART I.

Liquid Mixtures.

In the course of some work carried out in the chemical laboratory of the Johns Hopkins University and published under the title "The Conductivity and Viscosity of Solutions of Certain Salts in Mixtures of Acetone with Methyl Alcohol, Ethyl Alcohol and Water,"² it was observed that solutions of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, gave conductivities which were proportional to the amounts of the components of the mixture. In other words, when the conductivity curves were plotted they were found to be straight lines to within the limits of experimental error. When the fluidities of these solutions were found and plotted, similar results were obtained. It seemed possible, therefore, to explain the above changes in conductivity as due simply to changes in the fluidity of the solutions.

¹ The author is indebted to Prof. Joseph Ames and to Dr. H. Bradshaw for valuable suggestions and corrections.

² Jones and Bingham: *THIS JOURNAL*. 34, 481 (1905).

The viscosity curves for the above mixtures are sagged, *i. e.*, the viscosities of the mixtures are not directly proportional to the amounts of the components. Thus it seemed necessary to consider whether fluidities or viscosities are directly comparable with conductivities.

For this purpose it may be supposed that a mixture is made of two liquids which are composed of particles that have no unusual action upon each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids, which do not form complexes on mixing, would fulfil this condition. Further, it may be assumed that this mixture is allowed to flow through a tube. The more rapidly moving particles would be held back by those moving more slowly and the resulting motion would appear to be a mean value proportionate to the relative amounts of the components. In other words, the resulting fluidity would be the sum of the partial fluidities of the components. It should be noticed that this simple relation cannot be reasonably assumed when we consider viscosities instead of fluidities. Formulated, the above relation is

$$(m_1 + m_2)\Phi = m_1\phi_1 + m_2\phi_2 \dots \dots (1),$$

where m_1 and m_2 are the amounts of the components, ϕ_1 and ϕ_2 their respective fluidities and Φ the resultant fluidity.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors, in parallel, is represented by the sum of their separate conductances. The conductance of a pair of conductors, of different material, is, for a unit length,

$$(\sigma_1 + \sigma_2)C = c_1\sigma_1 + c_2\sigma_2,$$

where σ_1 and σ_2 are the areas of cross-section of the conductors, c_1 and c_2 their respective conductances, and C the resulting conductance.

If this reasoning is correct, conductivity and fluidity are strictly comparable.

It was stated above that it cannot be reasonably assumed that viscosities are additive. It is evident at once that, if fluidities are additive, viscosities cannot be additive. By

making m_1 and m_2 the amounts of the two components of a binary mixture, expressed in percentages, equation (1) becomes,

$$\begin{aligned}\Phi &= m_1\phi_1 + (1 - m_1)\phi_2 \dots \dots \dots (2), \\ &= m_1(\phi_1 - \phi_2) + \phi_2.\end{aligned}$$

If η_1 and η_2 represent the viscosities of the components and H that of the mixture, then, since viscosity is the reciprocal of fluidity, we have from (2),

$$\begin{aligned}\frac{1}{H} &= \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2} \\ \eta_1\eta_2 &= [m_1\eta_2 + (1 - m_1)\eta_1]H \\ &= [m_1(\eta_2 - \eta_1) + \eta_1]H.\end{aligned}$$

If we let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

we have

$$m'_1H = \frac{\eta_1\eta_2}{\eta_2 - \eta_1} \dots \dots \dots (3).$$

Since $\frac{\eta_1\eta_2}{\eta_2 - \eta_1}$ is a constant, equation (3) represents an equilateral hyperbola whose Y-axis is a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin to which equation (1) is referred. Thus we reach the conclusion that the hyperbola is the normal curve for the viscosities of simple mixtures.

Before this conclusion can be accepted as final, it will, of course, be necessary to show that, in a large number of cases, the fluidity curves of mixtures do in fact approximate to straight lines.

In the case of divergence from the straight line, it would be expected that new factors would be found entering to change the conditions. Such tendencies should manifest themselves in physical properties other than fluidity alone. It should be noted that, thus far, nobody has been able to establish any certain relations in mixtures between *viscosity* and other phys-

ical properties. The deviations in viscosity are quite uniformly greater than would be expected.

It has already been shown¹ that, in the particular case of water and acetone, there is a large deviation of the fluidity curve from a straight line. There is also a large contraction and evolution of heat on mixing. These phenomena seem to be general in the case of mixtures of water with other liquids. Traube² and others have studied a large number of such cases. In every instance there is a very great decrease in fluidity from what we should expect according to the rule of averages.

Unfortunately, there are no data relating to the other physical properties of these mixtures, hence it is impossible to use, in this connection, the data available. There exist, however, considerable data regarding the viscosity of non-aqueous mixtures. From these I have calculated the fluidities given in this paper. References to the sources of the material have been made in connection with the tables. Other data than those given have been considered, but, since no new relations were brought out, they have not been included here.

In Fig. I. and in Tables I. to VIII. are represented the fluidities of several pairs of liquids whose viscosity curves are only very slightly sagged. Ethyl acetate and carbon bisulphide, I., toluene and carbon bisulphide, II., toluene and ethyl acetate, III., form a trio of pairs of substances whose viscosity curves are very slightly sagged. On plotting the fluidities the curves closely approximate straight lines.

Benzene and toluene, IV., and benzene and chloroform, V., have viscosity curves which are almost identical and are nearly a straight line. The fluidities also give us a straight line, to the limits of experimental error. Since it is not practicable to draw two curves for the two pairs of substances, the points for the benzene and chloroform mixtures are indicated by crosses in the figure.

Benzene and chloroform, V, carbon tetrachloride and chloroform, VI., and carbon tetrachloride and benzene, VII., form a second trio of pairs whose fluidities are again very nearly proportional to the concentration of the components.

¹ Jones and Bingham: *THIS JOURNAL*, **34**, 540 (1905). Figs. XXI. and XXII.

² *Ber. d. chem. Ges.*, **19**, 871 (1886).

The above values have been taken from Linebarger.¹ Thorpe and Rodger,² commenting on his data, made the interesting observation that the viscosity curves approach straight lines when the viscosities of the components are not very different. In their own words, "As a rule, the greater the difference between the viscosities of the pure liquids, the greater is the difference between the calculated and the observed values of the mixtures." From the new point of view, the reason for this is immediately apparent. When η_1 and η_2 of equation (3) are nearly equal, the value of $\eta_2 - \eta_1$ is very small and the distance $\frac{\eta_1}{\eta_2 - \eta_1}$ becomes correspondingly great. The portion of the hyperbola, of which the observed viscosity curve forms a part, is, therefore, at a considerable distance from the vertex of the hyperbola, hence the curvature is small. We may get an idea of this distance from the figure by imagining the fluidity curves prolonged until they cross the X-axis. The point of intersection in each case will be the origin for the equilateral hyperbola of equation (3).

Table I.³—*Fluidity of Mixtures of Ethyl Acetate and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.000	0.00462	216.5
33.587	0.00416	240.4
60.754	0.00389	257.1
83.641	0.00367	272.5
100.000	0.00358	279.3

Table II.¹—*Fluidity of Mixtures of Toluene and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.000	0.00541	184.8
36.758	0.00469	213.2
62.008	0.00417	239.8
92.731	0.00370	270.3
100.000	0.00358	279.3

¹ Am. J. Sci., 2, 331 (1896).

² J. Chem. Soc., 71, 361 (1897).

³ Linebarger: Am. J. Sci., 2, 331 (1896).

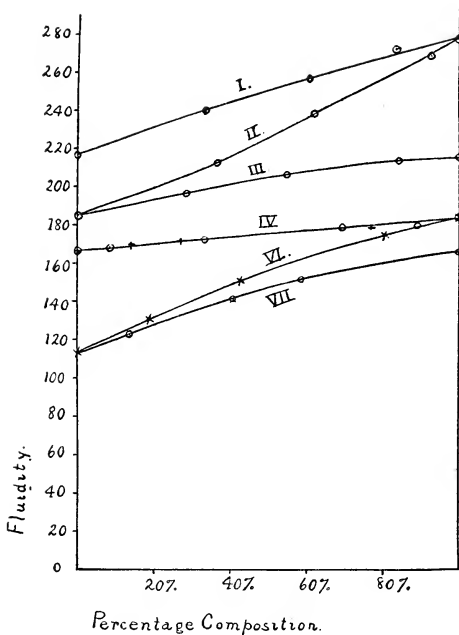


Figure 1.

- I. = Ethyl acetate and carbon bisulphide.
 II. = Toluene and carbon bisulphide.
 III. = Toluene and ethyl acetate.
 IV. = Benzene and toluene.
 V. = Benzene and chloroform.
 VI. = Carbon tetrachloride and chloroform.
 VII. = Carbon tetrachloride and benzene.

Table III.¹—Fluidity of Mixtures of Toluene and Ethyl Acetate at 25°.

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.000	0.00539	185.5
28.745	0.00509	196.5
54.699	0.00481	207.9
84.292	0.00466	214.6
100.000	0.00462	216.5

¹ Linebarger : Am. J. Sci., 2, 331 (1896).

Table IV.¹—Fluidity of Mixtures of Benzene and Toluene at 25°.

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.00599	166.9
8.444	0.00594	168.4
33.424	0.00579	172.7
69.412	0.00558	179.2
89.009	0.00555	180.2
100.000	0.00541	184.8

Table V.¹—Fluidity of Mixtures of Benzene and Chloroform at 25°.

Percentage of chloroform.	Viscosity.	Fluidity.
0.000	0.00599	166.9
14.169	0.00587	170.4
27.220	0.00581	172.1
76.990	0.00557	179.5
93.033	0.00546	183.2
100.000	0.00540	185.2

Table VI.¹—Fluidity of Mixtures of Carbon Tetrachloride and Chloroform at 25°.

Percentage of chloroform.	Viscosity.	Fluidity.
0.000	0.00883	113.25
18.828	0.00761	131.41
42.723	0.00659	151.75
80.731	0.00569	175.7
100.000	0.00540	185.2

Table VII.¹—Fluidity of Mixtures of Carbon Tetrachloride and Benzene at 25°.

Percentage of benzene.	Viscosity.	Fluidity.
0.000	0.00883	113.25
13.727	0.00808	123.76
40.780	0.00706	141.64
58.600	0.00660	151.52
100.000	0.00599	166.9

In Fig. 2 and in Tables VIII. to XIV. are represented the fluidities of several pairs of substances whose viscosity curves are considerably sagged. Figures showing the character of these viscosity curves have been published by Dunstan.² Ben-

¹ Linebarger: *Am. J. Sci.*, **2**, 331 (1896).

² *J. Chem. Soc.*, **85**, 821 (1904).

zene and ethyl acetate, VIII., nitrobenzene and ethyl acetate, IX., and nitrobenzene and benzene, X., form a third trio of pairs of substances. The second gives a curve that is somewhat sagged. The others are nearly straight. Ethyl alcohol and acetone, XI., give a straight line to the limits of experimental error. I have observed, moreover, that there is no perceptible contraction or evolution of heat on mixing these components. Turpentin and toluene, XII., and ethyl benzoate and toluene, XIII., give figures that are slightly curved but in opposite directions. In this connection it should be recalled that in certain cases there is a very marked change which takes place when two liquids are mixed, similar to that which is observed in all of the aqueous mixtures. Hence it would not be surprising if *no* two liquids give a curve that is absolutely a straight line; but when there are deviations in fluidity from the normal, there ought also to be evidence of abnormality in other physical properties. Since no such evidence is available in the above cases, we must be satisfied that the curves are approximately straight lines in such a large number of instances.

It will be helpful, at this point, to give some of the conclusions of previous workers on the viscosity observations, because considerations of fluidity throw some light upon those points that seemed quite obscure when viscosities alone were considered. Dunstan,¹ for example, remarks that "The law of mixtures is never accurately obeyed and divergences from it seem to be more clearly marked out in the case of viscosity than with other properties, such as refractive index." Thorpe and Rodger² say: "The observations described in this paper afford additional evidence of the fact indicated by Wijkander³ and supported by Linebarger,⁴ that the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition. It seldom happens that the liquid in a mixture preserves the particular viscosity it possesses in the unmixed condition. To

¹ J. Chem. Soc., 85, 819 (1904).

² *Ibid.*, 71, 374 (1897).

³ Lunds. Phys. Sällsk. Jubelskrift, 1878. Weid. Beibl., 8, 3 (1879).

⁴ Am. J. Sci., 11, 331 (1896).

judge from the instances heretofore studied, the viscosity of the mixture is, as a rule, uniformly lower than the mixture law would indicate, but no simple relation can yet be traced between the viscosity of a mixture and that of its constituents." They are so confident that there is some uncomprehended principle which causes the viscosity curve to always fall below the straight line, that they make the following statement¹ in regard to the viscosity curves of Linebarger, which *are* very nearly straight lines: "The observed viscosities in general are less than those calculated by the mixture rule, except, possibly, in the case of mixtures of benzene and chloroform and mixtures of carbon disulphide with benzene, toluene, ether and acetic ether, where, possibly, the temperature of observation (25°) was too near the boiling-point of the carbon disulphide to make any specific influence, which that liquid might exert at lower temperatures, perceptible." This assumption is not necessary according to the new view. Thus are explained not only the deviations from the values of the viscosities expected according to the rule of mixtures, but also even those perplexing cases where the rule is obeyed.

Table VIII.²—Fluidity of Mixtures of Benzene and Ethyl Acetate at 25°.

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.000	0.00599	166.9
19.197	0.00551	181.5
48.596	0.00487	205.3
84.406	0.00442	226.2
100.000	0.00434	230.4

Table IX.²—Fluidity of Mixtures of Nitrobenzene and Ethyl Acetate at 25°.

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.00	0.01834	54.52
24.47	0.01204	83.05
43.90	0.00889	112.49
77.10	0.00582	171.8
100.00	0.00434	229.9

¹ J. Chem. Soc., 71, 361 (1897).

² Linebarger: Am. J. Sci., 2, 331 (1896).

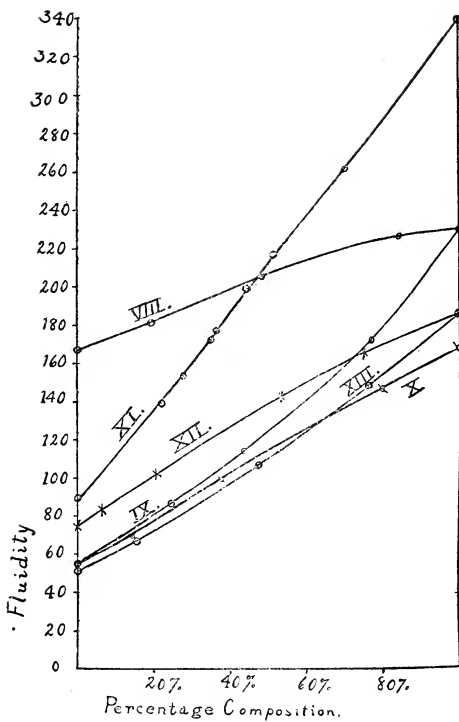


Figure 2.

- VIII. = Benzene and ethyl acetate.
 IX. = Nitrobenzene and ethyl acetate.
 X. = Nitrobenzene and benzene.
 XI. = Ethyl alcohol and acetone.
 XII. = Turpentin and toluene.
 XIII. = Ethyl benzoate and toluene.

Table X.¹—Fluidity of Mixtures of Nitrobenzene and Benzene at 25°.

Percentage of benzene.	Viscosity.	Fluidity.
0.000	0.01834	54.53
14.394	0.01417	69.58
37.610	0.01017	98.33
80.053	0.00681	146.8
100.000	0.00599	166.9

Table XI.¹—Fluidity of Mixtures of Ethyl Alcohol and Acetone at 25°.

Percentage of acetone.	Viscosity.	Fluidity.
0.00	0.01115	89.71
22.46	0.007168	139.50
27.77	0.006510	153.61
35.11	0.005797	172.3
36.83	0.005636	177.3
43.38	0.005162	193.7
44.50	0.005028	198.9
51.57	0.004620	216.5
70.34	0.003836	260.7
100.00	0.003125	320.0

Table XII.²—Fluidity of Mixtures of Turpentin and Toluene at 25°.

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.01343	74.47
6.791	0.01192	83.88
20.654	0.00978	102.2
53.701	0.00701	142.6
75.091	0.00607	164.7
100.000	0.00539	185.5

Table XIII.²—Fluidity of Mixtures of Ethyl Benzoate and Toluene at 25°.

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.01954	51.18
15.282	0.01495	66.89
47.322	0.00939	106.5
76.170	0.00679	147.3
100.000	0.00539	185.5

¹ Dunstan: J. Chem. Soc., 85, 822 (1904).² Linebarger: Am. J. Sci., 2, 331 (1896).

In Fig. 3, Tables XIV. to XVII., are represented another trio of pairs of substances—carbon bisulphide and ether, XIV., benzene and ether, XV., and benzene and carbon bisulphide, XVI. The curves for the first two are very nearly straight lines, that for the third is slightly sagged.

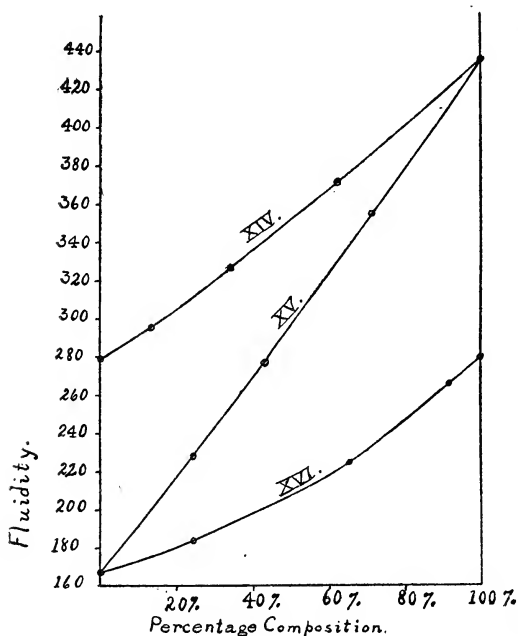


Figure 3.

- XIV. = Carbon bisulphide and ether.
XV. = Benzene and ether.
XVI. = Benzene and carbon bisulphide.

Table XIV.¹—Fluidities of Mixtures of Carbon Bisulphide and Ether at 25°.

Percentage of ether.	Viscosity.	Fluidity.
0.000	0.00358	279.3
13.100	0.00338	295.9
34.367	0.00306	326.8
62.759	0.00269	371.7
100.000	0.00230	434.8

Table XV.¹—Fluidity of Mixtures of Benzene and Ether at 25°.

Percentage of ether.	Viscosity.	Fluidity.
0.000	0.00599	166.9
24.309	0.00438	228.3
43.076	0.00362	276.2
71.424	0.00282	354.6
100.000	0.00230	434.8

Table XVI.¹—Fluidity of Mixtures of Benzene and Carbon Bisulphide at 25°.

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.000	0.00599	166.9
24.114	0.00544	183.8
65.142	0.00446	224.2
91.127	0.00376	266.0
100.000	0.00358	279.3

Fig. 4, Tables XVII. and XVIII., represent the fluidities of mixtures of methyl iodide and carbon bisulphide at 0°, 20° and 40°, and of carbon tetrachloride and benzene at 0°, 30° and 60°. The fluidity values for methyl iodide and carbon bisulphide mixtures are slightly greater than normally would be expected; but at low temperatures the effect is less marked. Now this increase in the fluidity may be explained as due to some change taking place when the components are brought together—perhaps a breaking down of a few molecular aggregations, which would naturally be facilitated by heat. This view accords with the facts and, fortunately, Thorpe and Rodger² furnish other data that support it. They found that when methyl iodide and carbon bisulphide are mixed an *expansion* occurs which is quite marked. With carbon tetra-

¹ Linebarger: Am. J. Sci., 2, 331 (1896).² J. Chem. Soc., 71, 367 (1897).

chloride and benzene there is also an elevation of the fluidity curves above the normal, but it is much less pronounced than in the previous case, especially at low temperatures. Thorpe and Rodger found that when carbon tetrachloride and benzene are mixed there is no expansion at all, but perhaps a very slight contraction.

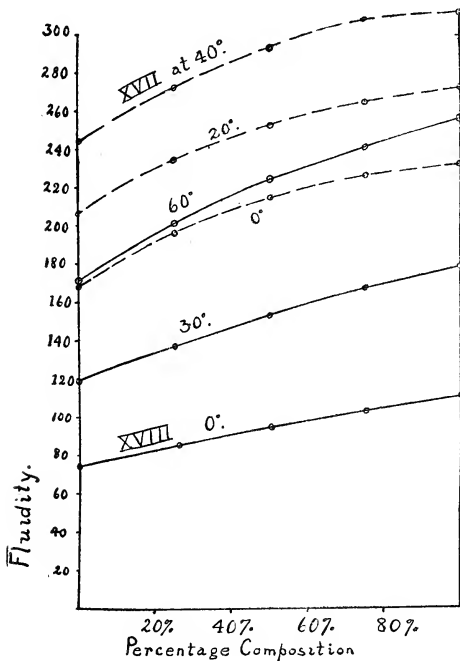


Figure 4.

XVII. = Methyl iodide and carbon bisulphide at 0°, 20° and 40°.
 XVIII. = Carbon tetrachloride and benzene at 0°, 30° and 60°.

Table XVII.¹—Fluidity of Mixtures of Methyl Iodide and Carbon Bisulphide at 0°, 20° and 40°.

Percentage of carbon bisulphide.	Fluidity at 0°.	Fluidity at 20°.	Fluidity at 40°.
0	168.1	206.6	244.5
25	196.5	234.2	272.1
50	214.6	252.5	293.3
75	226.2	265.3	307.7
100	232.6	273.2	312.5

Table XVIII.¹—Fluidity of Mixtures of Carbon Tetrachloride and Benzene at 0°, 30° and 60°.

Percentage of benzene.	Fluidity at 0°.	Fluidity at 30°.	Fluidity at 60°.
0	74.41	119.05	171.8
25	84.75	137.93	201.6
50	94.34	153.14	224.7
75	103.09	167.8	241.5
100	110.62	178.6	256.4

Fig. 5 represents the fluidities of chloroform and ether at 0° and 30°. In this case there is a pronounced sagging in the fluidity curve. The effect is less marked at the higher temperature. If the view which I suggest is correct, it must be assumed that when the chloroform and ether are mixed, a change takes place, which causes the fluidity to be abnormal. It is convenient to conceive of this as a tendency on the part of these liquids to form molecular aggregations with each other. Were these formed, they would be less stable at the higher temperatures and, consequently, the sagging would be less pronounced. This again accords with the facts, but Thorpe and Rodger¹ have furnished other data that are of interest. When chloroform and ether are mixed there is "a considerable evolution of heat and a notable contraction." They have measured this contraction at 0° for the four mixtures with which they worked. They found that the greatest contraction took place in the mixture containing 40.14 per cent of ether and 59.86 per cent of chloroform. On plotting the fluidities on a large scale and measuring the deviation

¹ Thorpe and Rodger: J. Chem. Soc., 71, 370, 366 (1897).

from the normal fluidity curve the maximum deviation is found to be most probably in a mixture containing 39 per cent of ether; but on account of the large degree of curvature and the scarcity of the determined points, it is impossible to locate the exact position of greatest deviation within some 3° of this value. On plotting the contractions in volume as ordinates and the percentage compositions as abscissae, the maximum contraction is seen to be most probably in a mixture containing less than 40 per cent of ether and perhaps less than 39 per cent. Here again, however, it is impossible to locate the exact point. Thus in the only case where the data are sufficient, there is a quantitative agreement between the abnormality in fluidity and volume.

It should be mentioned that the viscosity curves for this pair of substances show an inflection-point. To explain this according to the view that viscosities are additive, it was necessary to make two very doubtful assumptions.¹ According to the view here presented, only one new assumption is necessary, *viz.*, that there is a change which takes place when these components are mixed. This assumption has been shown to be entirely supported by the facts.

Chloroform and ether thus present a case exactly similar to what is found quite uniformly in aqueous mixtures, there being contraction, evolution of heat and a large decrease in fluidity, but in a less pronounced degree.

It was convenient to refer to this change as though due to molecular aggregations formed by the mutual action of the two liquids. In another connection the expression "breaking down of molecular aggregations" was employed. It is not intended by these phrases to introduce a theory as to the cause of the abnormality, the terms have been previously employed in viscosity discussions and are convenient as names for phenomena. It may be that the true explanation of the abnormality is more deep-seated, for if it is true that viscosity, in liquids, is dependent upon the attractions between the molecules, then, if, for any reason, there is a contraction on mixing two liquids, the molecules will be brought closer together than would

¹ J. Chem. Soc., 71, 374 (1897).

otherwise be expected and the attractions between the molecules will be increased. This will cause a decrease in the fluidity from the value calculated by the rule of mixtures. In a similar manner an expansion, on mixing the liquids, will cause an increase in the fluidity. Of course two liquids may form these molecular aggregates on mixing whenever there is a contraction, but there is no proof that the formation of such aggregates is necessary.

Ethyl alcohol and ethyl mercaptan, XX., give fluidities which are somewhat similar to those of chloroform and ether, but data in regard to other physical properties of these mixtures are not available.

Table XIX.¹—Fluidity of Mixtures of Chloroform and Ether at 0° and 30°.

Percentage of ether.	Viscosity at 0°.	Fluidity at 0°.	Viscosity at 30°.	Fluidity at 30°.
0.00	0.00700	142.9	0.00511	195.7
15.94	0.00678	147.5	0.00472	211.9
40.14	0.00562	177.9	0.00382	261.8
59.80	0.00440	227.2	0.00310	322.6
79.30	0.00350	285.7	0.00254	393.7
100.00	0.00286	349.6	0.00212	471.7

Table XX.²—Fluidity of Mixtures of Ethyl Alcohol and Mercaptan at 25°.

Percentage of mercaptan.	Viscosity.	Fluidity.
0.00	0.01113	89.5
3.48	0.01048	95.4
9.47	0.009731	102.8
12.30	0.009305	107.5
13.88	0.008559	114.2
16.25	0.008385	119.3
32.54	0.006525	153.2
35.97	0.006119	163.4
44.76	0.005821	171.8
68.05	0.004083	244.9
100.00	0.002091	478.2

¹ Thorpe and Rodger: J. Chem. Soc., 71, 373 (1897).

² Dunstan: *Ibid.*, 85, 821 (1904).

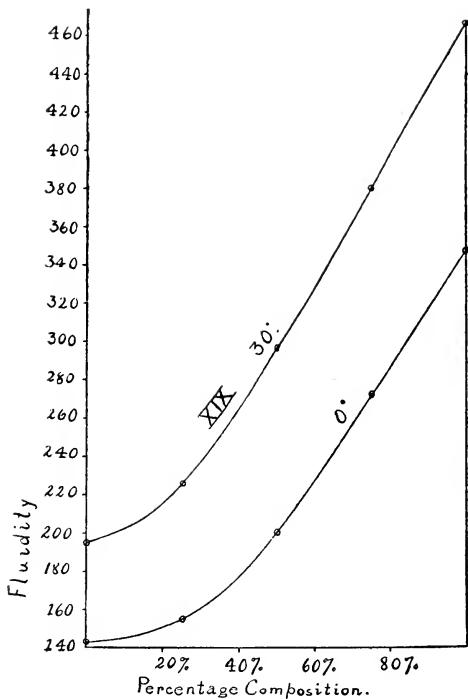


Figure 5.

XIX. = Chloroform and ether at 0° and 30° .

In Fig. 6 are shown three other examples of pairs of liquids which behave abnormally, but the data in regard to them is not sufficiently complete to furnish any new information. Ethyl alcohol and carbon bisulphide, XXI., give a considerably sagged curve; ethyl alcohol and benzene, XXII., show a sharp maximum in a 94 per cent mixture; benzaldehyde and ethyl alcohol, XXIII., also show a maximum in fluidity.

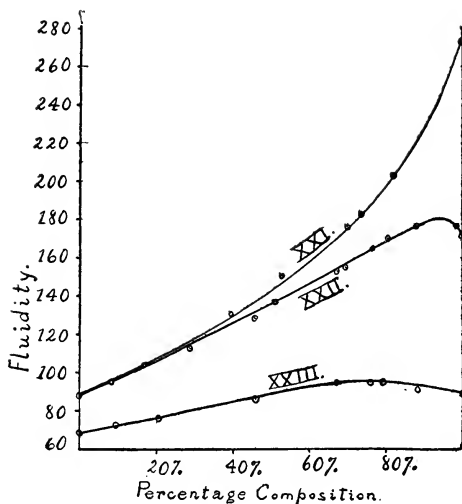


Figure 6.

XXI. = Ethyl alcohol and carbon bisulphide.

XXII. = Ethyl alcohol and benzene.

XXIII. = Benzaldehyde and ethyl alcohol.

Table XXI.¹—Fluidity of Mixtures of Ethyl Alcohol and Carbon Bisulphide at 25°.

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.00	0.01113	89.85
16.91	0.009448	105.84
19.29	0.009535	104.88
25.64	0.009065	110.32
32.31	0.008407	118.95
39.50	0.007621	131.21
52.82	0.006659	150.17
69.95	0.005669	176.35
73.50	0.005466	182.9
81.93	0.004926	203.1
100.00	0.003656	273.6

¹ Dunstan : J. Chem. Soc., 85, 820 (1904).

Table XXII.¹—*Fluidity of Mixtures of Ethyl Alcohol and Benzene at 25°.*

Percentage of benzene.	Viscosity.	Fluidity.
0.00	0.01130	88.50
8.47	0.01013	98.72
17.00	0.009545	104.77
28.90	0.008837	113.16
45.60	0.007758	128.89
50.91	0.007282	137.33
67.58	0.006514	153.52
69.49	0.006465	154.68
76.53	0.006071	164.71
80.38	0.005885	170.0
88.03	0.005669	176.2
98.86	0.005668	176.3
100.00	0.005821	171.8

Table XXIII.¹—*Fluidity of Mixtures of Benzaldehyde and Ethyl Alcohol at 25°.*

Percentage of ethyl alcohol.	Viscosity.	Fluidity.
0.00	0.01445	69.20
9.37	0.01362	73.42
20.68	0.01308	76.48
46.04	0.01158	86.36
67.53	0.01041	96.06
76.40	0.01051	95.15
79.33	0.01050	95.24
88.35	0.01092	91.58
100.00	0.01113	89.86

Previous observers, studying the viscosity of mixtures, expected to find the viscosity to be normally a linear function of the composition, but the exceptions were so frequent that they were assumed to be the rule. Nevertheless, there were a few perplexing cases where the viscosity did obey the mixture-rule. In this paper I have tried to show, from theoretical considerations, that *fluidities alone* should be additive and that the normal viscosity curve should be hyperbolic. I have also taken recorded viscosity data and shown that, *in a large number of instances, the fluidity curves of mixtures are nearly straight lines.* The viscosity data for aqueous mixtures have not been

¹ Dunstan : J. Chem. Soc., 85, 822 (1904).

considered here because, when water is mixed with other liquids, there evidently occurs some unusual change, for there is, in general, a contraction, an evolution of heat and a large decrease in fluidity. In the case of chloroform and ether a somewhat similar condition is observed. Thorpe and Rodger¹ found a considerable evolution of heat and a notable contraction. I have shown that there is a considerable sagging in the fluidity curve, and that the maximum deviation occurs in the mixture where there is the greatest contraction. Methyl iodide and carbon bisulphide expand on mixing and I have found that there is an increase in the fluidity over the values expected by the mixture-rule. Thus there seems to be a parallelism between the changes in fluidity and the other physical properties for which data are available.

The departures of the viscosity curves from the straight line are, therefore, satisfactorily explained and those cases which follow the mixture-rule are equally well explained. The inflection-point in the viscosity curve of chloroform and ether is also now accounted for in a manner which is in harmony with the facts.

I hope, later, to compare the fluidities of aqueous mixtures with various other physical properties, and to investigate more closely the cases which seem to show abnormality.

I have done a good deal of work upon the fluidities of pure liquids at different temperatures, using the elaborate viscosity data of Thorpe and Rodger.² The results will be communicated in a second paper. The relations are more interesting than those which appear with liquid mixtures, because any tendency on the part of two liquids to form molecular aggregates with each other is eliminated; the conditions are simpler and, therefore, a maximum in such fluidity curves would not be expected.

The curves are very nearly straight lines for all unassociated compounds and the fluidities of the compounds, in a homologous series, at any given temperature, decrease regularly as the molecular weight increases. Thus, when the fluidities are

¹ J. Chem. Soc., 71, 370 (1897).

² Phil. Trans., 185A, 307 (1894).

plotted as ordinates and the temperatures as abscissae, a series of nearly straight and parallel lines, inclined at a definite angle to the X-axis, are obtained. With associated compounds abnormalities appear, as would be expected. The fluidities of compounds in a homologous series, notably the acids, no longer increase regularly as the molecular weight increases. This is especially noticeable among the first members of the series. With the heavy alcohols, at low temperatures, the fluidity increases more rapidly than would be anticipated, the fluidity curves becoming fairly straight only at very high temperatures. This is in harmony with the theory of Kohlrausch¹ and Bousfield and Lowry,² that the fluidity of a liquid, on simple cooling, should never become zero, but asymptotic to the X-axis. Since the fluidity curve, at high temperatures, becomes nearly a straight line inclined at a definite angle to the X-axis, there is reason for supposing that the complete formula for the fluidity of a pure liquid at different temperatures would be a hyperbola. The formula of viscosity commonly used, $\eta = \frac{C}{1 + \alpha t + \beta t^2}$, where C , α and β are constants, tacitly assumes, however, that the fluidity curve has a parabolic form, since

$$\frac{1}{\eta} = \phi = (1 + \alpha t + \beta t^2)/C.$$

This leads, therefore, to the same conclusion that Kohlrausch³ reached by a different method, that this formula cannot express the viscosity relation over the widest possible range of temperature. An expression of the form

$$\phi = \frac{c}{\phi - at - b},$$

where c , a and b are constants would, apparently, be more suited to the theoretical requirements; it gives good results in certain cases that have been tested, when the values of the fluidities calculated are compared with those taken directly

¹ P. Roy. Soc., 71, 344 (1903).

² *Ibid.*, 70, 42 (1902).

³ *Loc. cit.*

from the viscosity observations. It is hoped that further work along this line will give some light on the association or molecular aggregations in pure liquids, which cause the bending of the fluidity curves.

LEIPZIG, September, 1905.

REACTIONS BETWEEN LEAD CHLORIDE AND LEAD ACETATE IN ACETIC ACID AND WATER SOLUTIONS.

BY JOHN WHITE.

The chloride, bromide, iodide and sulphate of lead, and perhaps other salts as well, dissolve much more readily in water solutions of the alkali acetates and tartrates than in water alone. In the case of the sulphate, this fact has long been known and made use of for purposes of analysis. Since the reactions have been but slightly studied, some time ago I began an investigation of them, with the object of determining their character, if possible. One paper upon the subject has already been published;¹ it dealt with the reactions between lead iodide and the acetates. Since then the work has been interrupted, and it has only recently been possible to take it up again.

Meanwhile certain confirmatory evidence as to the existence of compounds of the type described in the previous paper has been furnished through the work of Colson² on barium acetochloride, and of Lemoult³ on lead acetothiosulphate. In the present paper I shall endeavor to present additional evidence for the correctness of the formulas which have been suggested. No attempt has been made to formulate these compounds strictly in accordance with any of the existing theories of structure, because no definite information concerning their molecular complexity has, as yet, been obtained.

No very satisfactory explanation of the increased solubility of

¹ THIS JOURNAL, 31, 1 (1904).

² Compt. rend., 137, 660, 1061 (1903). Although the publication of Colson's article antedates mine, the latter had been written and was awaiting publication fully two months previous to the appearance of his.

³ *Ibid.*, 139, 422 (1904).

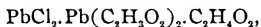
the lead salts in metallic acetates and tartrates has been offered ; the general assumption has been made that there is formed a complex ion,¹ containing lead. In a recent publication, Noyes and Whitcomb² have attempted to decide this question by studying the solubilities of lead sulphate in solutions of ammonium and sodium acetate and, as a result of conductivity and migration measurements, they have concluded that the increased solubility of the sulphate is due mainly to double decomposition, with the formation of unionized lead acetate. As between the suggested explanations, I have not been able to decide which the more correctly explains the increased solubility, but as a result of my own work, I am rather inclined to believe that, at least in some cases, the complex ion hypothesis more nearly represents the reaction which takes place. My previous work on lead iodide has shown that this dissolves in many of the metallic acetates with the formation of complex salts, which are either to be regarded as double salts pure and simple, or better, by assuming the intermediate formation of a complex ion, $\text{PbC}_2\text{H}_3\text{O}_2^+$, which is subsequently converted into the difficultly soluble complex salt. That metathesis may take place under certain conditions, I am prepared to admit, for I have found that, when lead chloride is dissolved in an aqueous or alcoholic solution of potassium or sodium acetate, the chlorides of potassium or of sodium can readily be obtained ; with ammonium acetate the reaction is quite different, for in this case I obtained beautiful crystals of the compound $2\text{PbCl}_2 \cdot 3\text{NH}_3$. It is evident, however, that when *lead* acetate is used as the solvent for the chloride, there can be no question of metathesis, yet the chloride of lead is distinctly more soluble in the acetate than in water. I have, moreover, succeeded in isolating some well defined products, which contain both the chloride and acetate of lead. It is possible that, with some other combination, Noyes and Whitcomb might have been led to a different conclusion.

I have found that the behavior of lead chloride toward lead

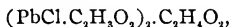
¹ Cf. Abegg and Herz: "Chemisches Praktikum," p. 68. Bailey and Cady: "Qualitative Analysis," p. 119. Kahlenberg and Shreiner: Z. physik. Chem., **17**, 577.

² J. Am. Chem. Soc., **27**, 747 (1905).

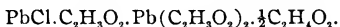
acetate is markedly influenced by the nature of the solvent used ; thus, in a glacial acetic acid solution of lead acetate, the chloride dissolves, forming characteristic crystals of the composition



or, as I prefer to express it,



while in water solutions a much more complex compound, of entirely different crystal form, is produced, *viz.* :



The latter is readily soluble in water and can be recrystallized undecomposed from such solutions, but it is quite easily decomposed by alcohol and acetic acid, yielding lead chloride, or intermediate compounds richer in chlorine than the original, while the former, though not soluble in cold acetic acid, is stable towards it, but is rapidly decomposed by water and alcohol. Rough quantitative experiments show that there is a certain minimum ratio which must hold between the acetate and the chloride, in order that the latter may be held in solution, this being, to some extent, independent of the actual concentration. In the acetic acid solution 1 molecule of chloride requires about 15 molecules of the acetate to hold it in solution, while in water solutions only 4 molecules are needed. A considerable variation of the amount of solvent was made in each case, without affecting the result other than changing the time required for crystallization to set in.

Solution of Lead Chloride in Acetic Acid Solution of Lead Acetate.—Appreciable amounts of lead chloride, especially if freshly prepared, dissolve when brought into a hot solution of lead acetate in glacial acetic acid. The proportions used should approximate to 18 grams of the acetate for each gram of the chloride ; the dilution mainly affects the time required for the crystals to separate. The following proportions were found to give a good yield within about 12 hours : Fifty grams of lead acetate in 60 to 70 cc. glacial acetic acid ; the boiling solution will dissolve about 2.7 grams of lead chloride, without subse-

quent separation. The crystals obtained in this case are quite large, with sharply defined angles; they were found to be prismatic crystals monoclinic in character.

Some difficulty was experienced for a time in finding a suitable medium for washing the crystals; alcohol was tried at first, since it did not appear to act very rapidly on them, but it was found that the analytical results, especially for chlorine, did not agree very well for the several preparations, and that they were affected by the length of time of the washing, so that it was concluded that, even in the cold and with rapid washing, using the pump, alcohol was not entirely without action; this was subsequently proven to be the case. Cold, glacial acetic acid was eventually made use of for washing and found to serve admirably, as there was practically no decomposition. Water decomposes the substance instantly. The general method of purification was to drain off the mother liquor by the aid of a pump, using a Witt filter, then wash thoroughly with glacial acetic acid, and place in a desiccator, over quicklime, for the removal of the excess of acetic acid.

It was discovered during the investigation that, in drying over lime, some difference was obtained if the substance was in the powdered condition, instead of the original coarse crystals, and that this difference was due, probably, to the loss of some acetic acid of crystallization after powdering. This was tested by drying some of the original crystals over lime for 4 days, when it was found that no odor of acetic acid could be detected. A portion of the crystals was powdered by grinding in an agate mortar, and the powdered portion then divided into two parts, the one was subjected to immediate analysis, the other replaced, together with the unpulverized substance, in the desiccator over lime. The odor of acetic acid became very pronounced upon grinding the crystals. The results of the analyses of the two portions are given below:

A.—Freshly Ground Portion.

0.1375 gram substance gave 0.1167 gram PbSO_4 .

0.4554 gram substance gave 0.1809 gram AgCl .

0.4080 gram substance gave 0.1882 gram CO_2 and 0.0678 gram H_2O .

B.—Pulverized Portion, Kept Over Lime 3 Days Longer (No Odor).

0.0945 gram substance gave 0.0816 gram PbSO_4 .

0.3970 gram substance gave 0.1602 gram AgCl .

0.3506 gram substance gave 0.1405 gram CO_2 and 0.0538 gram H_2O .

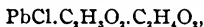
C.—Another Preparation, Ground and Kept Over Lime for Nearly 2 Weeks.

0.0473 gram substance gave 0.0413 gram PbSO_4 .

0.2626 gram substance gave 0.1057 gram CO_2 and 0.0385 gram H_2O .

It was found that the original crystals could be kept for some time over lime without suffering change, although they lose acetic acid very slowly.

Numerous preparations, made under varying conditions, led to similar results, and to the conclusion that the freshly crystallized salt has a composition corresponding to the formula



but that it has a tendency to lose a portion of its acid of crystallization upon standing, especially when in the pulverized state. Attempts to determine the acetic acid directly, by heating, were unsuccessful; constancy of weight could not be obtained, owing probably to a deeper seated decomposition taking place.

The following tabular representation will serve to show the change occurring, due to loss of acetic acid:

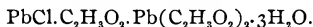
	Calculated for			Found.	
	$\text{PbCl} \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$	$\text{PbCl} \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$	A.	B.	C.
Pb	57.25	62.43	57.96	58.97	59.63
Cl	9.81	10.69	9.82	9.98	. .
C	13.28	10.86	12.58	10.92	10.98
H	1.95	1.52	1.86	1.72	1.64

Carius¹ has described a compound similar to the above, but

¹ Ann. Chem. (Liebig), **125**, 87 (1863).

without acetic acid of crystallization, which he prepared by heating a mixture of ethylene chloride, lead acetate and acetic acid, in a sealed tube, at 180° . I have made numerous efforts to prepare the substance by Carius' method, but have in no case obtained a compound which did not consist mostly of lead chloride. Neither was I able to confirm his statement that the salt, when treated with water, is decomposed first to a white powder, which gradually goes into solution, forming a complex salt soluble in water. I found that water effects an instant and complete decomposition of the substance, forming lead chloride, but could detect no subsequent tendency for this to redissolve.

The Salt Formed in Aqueous Solution of Lead Acetate.—Carious¹ has already shown that lead chloride dissolves in an aqueous solution of lead acetate, forming a crystalline compound, to which he ascribed the formula



It is quite probable, from the method of procedure described, that the product obtained by him was somewhat impure, hence it was decided to repeat the experiments.

Roughly quantitative measurements indicate that 1 molecule of lead chloride requires 4 molecules of lead acetate to effect its solution, and that this ratio is not materially affected by using, instead of water, dilute alcohol, 60–70 per cent. In practice it has been found that water containing a little acetic acid serves best as solvent and that the following proportions give the quickest separation of crystals and the best yield: One hundred cc. water, 1–2 cc. acetic acid, 25–27 grams lead acetate and 5 grams lead chloride, the solution taking place at the boiling temperature. Under these conditions there is no separation of lead chloride upon cooling, and the crystals of the substance formed separate out as a thick mass, consisting of radiating tufts of fine, silky needles. The conditions of formation were varied for the different preparations within quite wide limits, without affecting the result.

The crystals are quite easily soluble in cold water, but if the

¹ *Loc. cit.*

solution is made too concentrated some decomposition ensues, with precipitation of lead chloride. I have usually purified the substance for purposes of analysis by draining off the mother liquor as completely as possible by means of the pump, washing rapidly with several portions of cold water, then recrystallizing it by dissolving the solid in cold water, containing a drop of acetic acid,¹ to make a dilute solution. This solution was allowed to evaporate slowly over strong sulphuric acid until the crystals began to appear. Occasionally lead chloride in small amount separated out, especially if the original solution was too concentrated, this was filtered off. The crystals obtained in this way are very long, but of too small cross-section to permit of a determination of their crystal form. The following will serve as a typical analysis of a doubly recrystallized salt, dried *in vacuo*, over sulphuric acid :

0.0707 gram substance gave 0.0646 gram $\text{PbSO}_4 = 62.40$ per cent Pb.

0.3311 gram substance gave 0.0744 gram $\text{AgCl} = 5.55$ per cent Cl.

0.2710 gram substance gave 0.1051 gram $\text{CO}_2 = 10.58$ per cent C.

0.2710 gram substance gave 0.0454 gram $\text{H}_2\text{O} = 1.88$ per cent H.

A number of preparations and analyses were made with the object of definitely determining which of the three following possible formulas is to be ascribed to the salt, *viz.* :

	I. $\text{PbCl} \cdot \text{C}_2\text{H}_3\text{O}_2$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	II. $\text{PbCl} \cdot \text{C}_2\text{H}_3\text{O}_2$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	III. $\text{PbCl} \cdot \text{C}_2\text{H}_3\text{O}_2$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$
Pb	64.22	62.47	63.04
Cl	5.50	5.35	5.40
C	10.70	10.87	12.81
H	1.71	1.98	1.69

It will be seen that, with the exception of the lead in I. and the carbon in III., there is very little difference in the percentages required for the three, the difference, in no case, being sufficient

¹ Water alone may be used, but unless freshly boiled, the carbon dioxide present will produce a cloudiness, which is prevented by the use of acetic acid.

to allow of a positive decision between them based upon analysis. In the table below are given the individual determinations of the several constituents, together with the mean value in each case. These represent a number of different preparations :

Pb.	Cl.	C.	H.	Mean value.	
62.80	5.61	10.53	1.73	Pb	63.05
62.85	5.60	10.47	1.85	Cl	5.56
63.25	5.64	10.58	1.88	C	10.70
63.51	5.55	10.82 ¹	1.52 ¹	H	1.71
62.72	5.53	11.12 ¹	1.57 ¹		
63.15	5.44				

From the values obtained, it is not definitely certain which of the three proposed formulas is to be ascribed to the salt. An attempt at drying, with the object of determining by loss the amount of water or of acetic acid of crystallization, led to no very satisfactory result. The sample lost 5.13 per cent in weight after drying for 6 hours at 104°, but absolute constancy of weight could not be obtained, although the loss, after drying for 3 hours, was very slow. This is contrary to the experience of Carius,² who states that the water of crystallization could be easily determined by drying at 100°. Assuming the loss found, *viz.*, 5.13 per cent., to be approximately correct, this might equally well be taken as proving either Formula II. or III., the first of these requiring a loss of 5.44 per cent, the latter 4.56 per cent. One sample which had stood for nearly 3 months in a desiccator, over concentrated sulphuric acid, gave, upon analysis, 5.55 per cent of chlorine and 1.52 per cent of hydrogen, thus showing that no very marked loss of water, or of acetic acid, takes place under these conditions.

Since the compound is readily soluble in water, an attempt was made to solve the problem of its formula, as well as that of similarly constituted compounds, by making a molecular weight determination, using the freezing point method. The results are given below. I., II. and III. here refer to separate preparations of the salt :

¹ These results were obtained with a sample that had been kept in a desiccator, over sulphuric acid, for several months; it may have suffered slight change.

² *Loc. cit.*

Solvent Water—Molecular Lowering 1850.

	Weight of substance. Gram.	Weight of water. Grams.	Freezing point of water.	Freezing point of solution.	Depression.	Molecular weight.
I.	0.1611	14.81	2°.286	2°.162	0°.124	162.3
	0.1979	"	"	2°.135	0°.151	163.7
II.	0.1065	12.93	4°.227	4°.136	0°.091	167.4
III.	0.1317	12.77	4°.383	4°.273	0°.110	173.4

The molecular weight found, 166.7 (average), being very nearly one-fourth that required for any one of the proposed formulas, may be regarded either as indicating a resolution of the substance into 4 simpler molecules or ions, *i. e.*, indicating dissociation, or that the lowering is caused entirely by lead acetate, mol. wt. = 162.4. The latter assumption, if true, might be taken as indicating the correctness of Formula III., for this can really be considered as consisting of 2 molecules of lead acetate plus 1 atom of chlorine, the additional weight of which would probably not be detected by this method of determining molecular weights.

On looking through the literature, I found one other salt of similar composition which is soluble. This is the calcium acetochloride, $\text{CaCl} \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 5\text{H}_2\text{O}$, which has been described by Fritsche.¹ I prepared the salt according to his directions, and obtained it in beautiful crystals, the analysis of which agreed well with the formula. This substance is easily soluble in water, and with it I made three molecular weight determinations, which gave 89, 85 and 87, respectively. This is approximately one-half of that required for a compound of the above formula. Here again it appears that, in water solution, some sort of dissociation takes place, the nature of which is not quite clear.

The molecular weight determinations of the salt have, therefore, not been of such character as to enable me to decide definitely what its true formula is, but they point, perhaps, more towards the correctness of the formula which has acetic acid of crystallization. It may be that, later, some more suitable solvent can be found, in which no dissociation takes place and in which the molecular weight can be definitely determined.

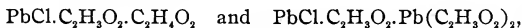
¹ Pogg. Ann., 28, 121 (1833).

The salt is, as stated, soluble in cold water, but decomposes to a considerable extent in hot water; cold alcohol exerts a slow decomposing action, hot alcohol a much more rapid decomposition, both, apparently, extracting lead acetate, leaving a crystalline residue richer in chlorine. In one case, after extracting with hot alcohol, it was found that the residue contained 13.64 per cent of chlorine, which, after a second extraction, was found to have increased to 19.89 per cent. When the alcohol has dissolved enough of the acetate to bring the ratio between it and lead chloride up to the required amount, some of the latter dissolves, for it was found that, by evaporating the filtrate, a salt of the original composition was obtained. Acetic acid is very much more active than alcohol, producing instantaneous decomposition, with precipitation of lead chloride. Melting point determinations were unsatisfactory, the substance softens at 83° , but does not melt to a transparent liquid until a temperature of about 193° has been reached. There is some darkening of the mass at this point and gas is evolved, showing decomposition.

Summary.

1. A study of two complex salts containing chlorine has been made; one of these is produced when lead chloride is dissolved in a hot acetic acid solution of lead acetate; the other by use of a water solution of the acetate.

2. The probable formulas deduced for these, based upon analyses, are, respectively:



the latter crystallizing either with water or acetic acid of crystallization.

3. The results indicate, therefore, that the nature of the solvent plays an important part in determining the composition and character of the salt formed. This appears to be one influencing the complexity, or association of the molecules, rather than the nature of the reaction, which is of the same general character in both solvents.

4. Molecular weight determinations of the second compound

mentioned above gave values approximately one-fourth the molecular weight calculated, indicating a probable dissociation; the same was found to be true for the compound $\text{CaCl}_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 5\text{H}_2\text{O}$, which has been previously described by Fritsche.

5. Lead chloride forms compounds with lead acetate analogous to those previously described for the iodide, but its action towards the alkaline acetates is quite different, the chloride undergoing double decomposition in solutions of these, the iodide, on the other hand, combining with them in the same manner as with the lead acetate.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, Oct., 1905.

A STUDY OF THE REACTIONS INVOLVED IN THE FORMATION OF CERTAIN COMPLEX SALTS OF LEAD.

BY JOHN WHITE AND J. M. NELSON.

It has been previously shown by White¹ that certain difficultly soluble salts of lead, such as the iodide, chloride, etc., are soluble, to a remarkable degree, in aqueous or alcoholic solutions of metallic acetates. In offering an explanation of this fact, White assumed that the salts of lead, like those of a number of other bivalent metals, ionize in two stages, the first stage taking place more readily than the second in solutions of moderate concentration. Through the action of other salts, *e. g.*, the metallic acetates, during the first stage, it is possible to conceive of the formation of a mixed salt of the type $\text{PbX} \cdot \text{C}_2\text{H}_3\text{O}_2$. As a proof of this view, a number of salts referable to this type have been prepared, by dissolving the halogen salts of lead in solutions of the metallic acetates.

Carius² has described several salts of the simple type mentioned above, but in the course of the work carried out by White, it was observed that the tendency has been rather to form salts somewhat more complex than that. This was especially the case with the iodides, and the experiments de-

¹ THIS JOURNAL, 31, 1 (1904). Cf. preceding article.

² Ann. Chem. (Liebig), 56, 234 (1845).

scribed in the present paper were undertaken for the purpose of studying the reactions somewhat more closely with the hope of obtaining additional information upon the subject. The object being the preparation, if possible, of the simple compound $\text{PbI.C}_2\text{H}_3\text{O}_2$, it was thought that this might be the more easily accomplished by the use of the method described by Carius, *viz.*, by heating together mixtures of lead acetate and an alkyl iodide, using a suitable solvent. It was soon discovered that the nature of the solvent had to be taken into account, as the reactions do not proceed in the same way in solvents that are markedly different in general properties.¹ Glacial acetic acid was first used, this being the solvent employed by Carius; the present paper deals more especially with reactions in this solvent.

Numerous repetitions of the experiments of Carius, following the conditions stated by him, *viz.*, with ethyl iodide and lead acetate, mixed in the proportion of 1 molecule of each, dissolved in 1 molecule of acetic acid and heated in a bomb-oven to 140° , have resulted always in failure, lead iodide being, in every case, the principal product. A study of the conditions has led to the conclusion that a larger amount of lead acetate is needed at this temperature to prevent the formation of the iodide, and that, at much lower temperatures, a reaction takes place, with the production of complex salts closely allied to the compound $\text{PbI.C}_2\text{H}_3\text{O}_2$. This compound itself has not yet been obtained. We believe the reason to be either the greater ease of decomposition of the iodine salts or the greater reactivity (more ready ionization) of the iodine compounds, because, in the preceding paper, it has been shown that the chlorine compound probably exists.

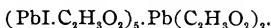
Instead of using the bomb-oven as described by Carius, we have found it more convenient to carry out the reactions described in this article by heating the requisite amount of lead acetate, alkyl iodide and acetic acid, enclosed in a short sealed tube, bound to the axle of a rotating device within a water-bath. In this way the contents of the tube could be kept constantly stirred, a necessary precaution, because it was found

¹ *Vide* preceding paper.

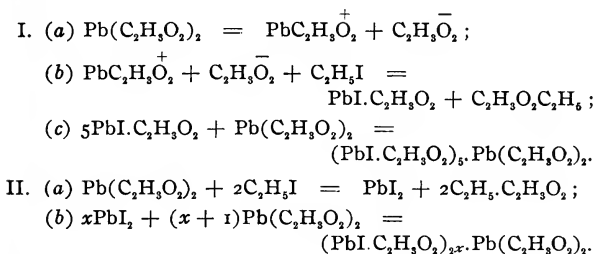
that it serves in large measure to prevent the formation of lead iodide, while at the same time it served as a stirrer for the water in the bath.

The results showed that the reaction which takes place under these conditions is of a somewhat complex character, and that its exact nature could not be determined. Something was, however, learned regarding the influences operating to produce the reaction and, incidentally, sufficient information was acquired to permit us to draw certain inferences regarding its general trend. This will appear in the experimental work following. The temperature is an important factor, as was to be expected, since it influences the degree of dissociation and, consequently, the active mass of the dissolved substances, which are also, to some extent, although not so markedly, affected by varying the relative proportions of the solvent and of the reacting substances.

Contrary to our hope that we might obtain the lead aceto-iodide only, we found that the principal product is a complex salt of the general character of those previously described by White and corresponding to the hypothetical formula,



The formation of such a salt may be explained theoretically in one of two ways, represented by the following sets of equations:

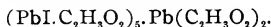


The result is, naturally, the same in either case, although the intermediate stages vary considerably. It was in the endeavor to decide between these that the experiments described

below were undertaken. The general result seems to be rather in favor of the first set of reactions. It is certain that, under suitable conditions, a white, crystalline salt can be obtained directly and without any indications of an intermediate formation of lead iodide, thus pointing to the correctness of the first set of reactions. Moreover, in those instances where lead iodide was formed, the conditions were such as to favor the decomposition of the unstable compound, $\text{PbI.C}_2\text{H}_3\text{O}_2$, assuming it to be the first product of the reaction, into the iodide and acetate of lead.

The facts observed during the course of the investigation seem to be in harmony with this assumption. Such being the case, the following may serve as an explanation of what was observed to take place during the several experiments to be described below :

The temperature must, of necessity, exert a marked effect upon the reaction, for an increase of temperature would naturally increase the tendency of both reactions, (a) and (b), to take place, since it would produce an increase in the degree of dissociation of the lead acetate,¹ and likewise in the reactivity of the alkyl halide.² At the same time this increase in temperature would have a marked tendency to cause a decomposition of the rather unstable substance $\text{PbI.C}_2\text{H}_3\text{O}_2$, forming lead iodide (*vide* Exps. 1 and 2). This formation of lead iodide could only be prevented by increasing the amount of lead acetate, so as to cause the removal of the iodine from the solution in the form of the difficultly soluble salt,



It is, therefore, to be expected that for a given initial amount of the reacting substances, there is a certain maximum, beyond which the temperature cannot be raised, without giving rise to the formation of lead iodide. This is in entire accord with our observations.

An increase in the amount of alkyl halide, or a decrease in

¹ It is probably in connection with this that the nature of the solvent has to be taken into account, since this would naturally have an effect upon the dissociation of the lead salt.

² Slator (J. Chem. Soc., 85, 1286 (1904)) has shown that the effect of temperature is very marked, a rise of 10° trebles the velocity of the reaction.

the amount of lead acetate, would, according to the law of mass action, tend to increase the amount of acetoiodide formed and, in the absence of a sufficient excess of lead acetate, also the decomposition of this into lead iodide (*vide* Exps. 6 and 7). For a given temperature the particular alkyl halide used will also, in a measure, determine whether or not the iodine will stay in the solution or be precipitated as lead iodide; ethyl iodide, for instance, being considerably less reactive at a given temperature than methyl iodide,¹ may be used at higher temperatures than the latter without giving rise to the formation of lead iodide (*vide* Exps. 8 and 9).

Increasing the amount of the solvent acetic acid would affect the trend of the reaction in several ways; it would decrease the concentrations and, consequently, the active masses of the reacting substances and, unless this effect were equal in degree for both, the whole reaction would be affected; in addition, the increase in solvent would have a marked decomposing effect upon the acetoiodide formed, tending, therefore, to the formation of lead iodide² (*vide* Exps. 3, 4 and 5).

It is, of course, not impossible to interpret the results in such a way as to make them conform to the set of reactions designated as II. No very definite proof can be furnished indicating which of the sets of reactions is to be regarded as the correct one, but the facts are so easily explained by the former set that we feel inclined, in the absence of contrary evidence, to accept this in preference to the other.

EXPERIMENTAL.

Preparation of the Salt, $(\text{PbI.C}_2\text{H}_3\text{O}_2)_5.\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.—Six grams of methyl iodide, 12 grams of lead acetate, about 1 molecule of each, 4 cc. of acetic acid and 4 cc. of acetic anhydride³ were brought together in a sealed tube. After heating at 98°, for an hour, a white, crystalline substance began to separate. The heating was continued at the same temperature for about 7 hours, the tube was then removed from the

¹ Slaton: *Loc. cit.*

² *Vide* White's "Experiments with the Iodides," *loc. cit.*

³ The lead acetate not being completely dehydrated, a little acetic anhydride was added to take up the water and prevent the formation of basic iodide.

bath and opened, the crystals filtered upon a Witt plate and examined under the microscope; they appeared homogeneous throughout and were monoclinic. They were washed with cold alcohol, which does not exert a very rapid decomposing action upon them and then dried in a partial vacuum, over concentrated sulphuric acid. Analysis:

	Calculated for (PbI.C ₂ H ₃ O ₂) ₅ .Pb(C ₂ H ₃ O ₂) ₂ .	Found.
Pb	54.23	53.94
I	27.71	27.53
C	7.34	7.18
H	0.92	0.88

Preparation 2.—The proportions were the same as in the first preparation; the temperature was, however, considerably lower, 70° instead of 98°. After 4 hours, lead iodide began to form. The tube was opened, the liquid filtered from the lead iodide and poured into a flask, which was then allowed to stand on a steam radiator for about 10 hours, after which time white crystals formed at the bottom of the flask, with a ring of lead iodide around the flask at the top of the liquid. The crystals, which were quite large, were removed from the flask mechanically and were washed and dried as in the previous case. Analysis:

	Calculated for (PbI.C ₂ H ₃ O ₂) ₅ .Pb(C ₂ H ₃ O ₂) ₂ .	Found.
Pb	54.23	53.98
I	27.71	27.37
C	7.34	7.43
H	0.92	0.89

Preparation 3.—Six grams of methyl iodide (1 mol.), 10 grams of lead acetate (0.75 mol.), 6 cc. of acetic acid and 2 cc. of acetic anhydride were heated as in the preceding preparations. The temperature of the bath was kept between 60° and 70°. After 6 hours a very good crop of white crystals had separated; they were removed from the tube and showed, under the microscope, the same crystal form as those obtained in the previous preparations. No lead iodide was observed in this case during the reaction. The crystals were washed with alcohol and dried over sulphuric acid for analysis:

	Calculated for (PbI.C ₂ H ₃ O ₂) ₆ .Pb(C ₂ H ₃ O ₂) ₂ .	Found.
Pb	54.23	54.55
I	27.71	27.35
C	7.34	7.13
H	0.92	0.92

Having thus demonstrated the existence of a definite compound, as shown by the analysis of the various preparations, the following set of experiments were undertaken with the object of making a closer study of the causes operating to influence the trend of the reaction :

Influence of Temperature.

Exp. 1.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportions 2 : 1, 2 cc. of acetic acid and 2 cc. of acetic anhydride were used. The temperature of the bath was maintained at 85°. The solution remained clear for about 3 hours, when the formation of lead iodide began.

Exp. 2.—The same amounts of substances were used as in the preceding case, but the temperature was 70°. The solution remained clear for about 2 hours, when the white crystals began to deposit.

It appears, from the above, that the temperature has a marked effect upon the reaction and that for these proportions of the reacting substances it must not be allowed to exceed 70°–75°, if it is desired to prevent the formation of lead iodide. When other proportions were used similar results were obtained.

Influence of Acetic Acid.

Exp. 3.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 16 cc. of acetic acid and 4 cc. of acetic anhydride, were heated for 2.5 hours, at about 85°–90°. Lead iodide was formed toward the latter part of the operation.

Exp. 4.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 12 cc. of acetic acid and 4 cc. of acetic anhydride were used. The temperature was 85°–90°. Lead iodide began to form after about 3 hours.

Exp. 5.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 4 cc. of acetic acid and 4 cc. of acetic anhydride were heated to 98°. No lead iodide was formed, instead only the white, crystalline salt.

It appears that, for a given proportion of the other constituents and at a certain temperature, there is a limit to the amount of acetic acid which can be used, if the complex salt is desired.

Influence of Lead Acetate.

Exp. 6.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 2 cc. of acetic acid and 2 cc. of acetic anhydride were maintained at 85°, for 3 hours, when the formation of lead iodide was observed.

Exp. 7.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 4 cc. of acetic acid and 4 cc. of acetic anhydride were heated at 98°. No lead iodide separated out, instead only the white salt. It will be observed that, in this case, the proportion of acetic acid had been increased, also the temperature, which would both tend to the production of lead iodide, but the increase in the proportion of the acetate more than offset this tendency. The two experiments, taken together, show that lead acetate, when in sufficient excess, has a very strong influence in preventing the formation of lead iodide.

Influence of Alkyl Halide.

Exp. 8.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 8 cc. of acetic acid and 2 cc. of acetic anhydride were heated at 70° for a short time, when lead iodide was formed.

Exp. 9.—Six grams of ethyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 8 cc. of acetic acid and 2 cc. of acetic anhydride were heated at 70°, for some time. No lead iodide was formed, the white salt being obtained instead.

In this case it is evident that the methyl iodide, being more active at a given temperature than ethyl iodide, is more likely to cause the formation and separation of lead iodide.

Summary.

1. A new salt of the same general character as those previously described has been prepared and studied. This salt, however, is different in composition and, to some extent, in properties, from that previously obtained by dissolving lead iodide in an acetic acid solution of lead acetate.

2. The simple compound $\text{PbI.C}_2\text{H}_3\text{O}_2$ could not be obtained.

3. It has been found that the reaction is influenced by changes of temperature, concentration and the relative proportions of the reacting substances.

4. From this it is possible to gain some insight into the nature of the reaction. While not definitely proven, all the facts observed apparently point to the conclusion that an intermediate compound, $\text{PbI.C}_2\text{H}_3\text{O}_2$, is formed.

Up to the present time the following salts have been obtained :

Simple salt.	Molecular proportions.
	I : I
$\text{PbCl.C}_2\text{H}_3\text{O}_2$	$\text{PbCl.C}_2\text{H}_3\text{O}_2.\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2.\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$
	$\text{PbI.C}_2\text{H}_3\text{O}_2.\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2.\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$
	$\text{PbI.C}_2\text{H}_3\text{O}_2.\text{NaC}_2\text{H}_3\text{O}_2.\frac{1}{2}\text{C}_2\text{H}_3\text{O}_2$
	Without acetic acid.
	$\text{PbI.C}_2\text{H}_3\text{O}_2.\text{KC}_2\text{H}_3\text{O}_2$
	$\text{PbI.C}_2\text{H}_3\text{O}_2.\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
	More complex salts.
	$\text{PbI.C}_2\text{H}_3\text{O}_2.(\text{NaC}_2\text{H}_3\text{O}_2)_3.\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$
	$(\text{PbI.C}_2\text{H}_3\text{O}_2)_5.\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$

The bromine compounds are at present under investigation, and it is the intention to take up the sulphate, and possibly some others, in the near future.

THE DOUBLE SALTS OF MERCURIC CHLORIDE WITH THE ALKALI CHLORIDES AND THEIR SOLUBILITY.

BY H. W. FOOTE AND L. H. LEVY.

In a previous article by one of us,¹ the double caesium mercuric chlorides were determined by what we shall call the solubility method and found to be the same as those described by Wells.² The advantages of the method we used are that all stable salts, forming at a given temperature, can be determined with a good degree of certainty and that the solubility conditions under which each salt forms are ascertained. The method has already been applied to several series of double salts besides the caesium mercuric chlorides.³ The method used in the present article is essentially the same that has been used before. Varying mixtures, carefully weighed, of mercuric chloride and an alkali chloride were treated with hot water enough to dissolve them, placed in the thermostat at 25° and shaken, usually for several days. Weighed quantities of solution were then removed through a filter of glass wool and analyzed. The residues were dried as quickly as possible between filter paper and analyzed by the same method used for the solutions.

The analyses were carried out by precipitating mercuric sulphide from the solution acidified with hydrochloric acid, filtering on a Gooch crucible, drying at 100° and weighing the mercuric sulphide. The filtrate from the sulphide was evaporated and the residue weighed as chloride.

A series of two or more results giving a constant composition of the residue and varying solubility shows a pure double salt to be present, while constant solubility and varying residue indicates a mixture of two salts.

POTASSIUM MERCURIC CHLORIDES.

BY H. W. FOOTE.

Three double potassium mercuric chlorides have been de-

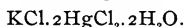
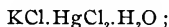
¹ THIS JOURNAL, 30, 339.

² Am. J. Sci., 44, 221 (1892).

³ THIS JOURNAL, 30, 330; 32, 246, 251; 34, 153, 164.

scribed by Bonsdorf¹ and we have found the same ones at 25°.

These salts are :



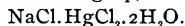
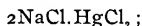
The results obtained are given below. Constant composition of the residues, showing a pure double salt, is italicized. The solubility of pure potassium chloride was determined by Mr. J. G. Stathiropoulos in duplicate from two solutions, one of which was first supersaturated and the other undersaturated, at 25°.

The analyses of the residues in Nos. 10-14 vary considerably, although the pure 1 : 1 salt was present. This was because the salt crystallized as a mass of silky needles which it was impossible to dry properly.

SODIUM MERCURIC CHLORIDES.

BY H. W. FOOTE.

Two sodium mercuric chlorides have been described by Bonsdorf² and others. They have the formulas :



We have been unable to detect the first salt at either 25° or 10°.3.

The results obtained at 25° are given in Table II.

The results show clearly that the salt $\text{NaCl}.\text{HgCl}_2.2\text{H}_2\text{O}$ is present, but show no indication of $2\text{NaCl}.\text{HgCl}_2$. The latter salt contains 69.84 per cent of mercuric chloride. Had this salt formed, the solubility results in Nos. 1-3 of the following table, corresponding in composition to a mixture of NaCl and the 2 : 1 compound would have been different from the solubility in No. 4, corresponding to a mixture of 2 : 1 and 1 : 1 derivatives. That the results are the same shows that this salt has not been produced, but that the residues in the four results consist of a mixture of the same salts.

¹ Pogg. Ann., 17, 115.

² Loc. cit.

Table I.—*Solubility of Potassium and Mercuric Chlorides at 25°.*

No.	Per cent KCl in solution.	Per cent HgCl ₂ in solution.	Per cent KCl in residue.	Per cent HgCl ₂ in residue.	Residue contains:
0	26.46	none	100	none	KCl
1	26.24	15.04	..	3.63	KCl and 2KCl.HgCl ₂ .H ₂ O
2	26.43	15.02	..	26.15	
3	26.33	15.02	..	52.01	
4	26.33	14.92	..	61.04	
5	23.74	18.91	34.61	61.66	2KCl.HgCl ₂ .H ₂ O
6	22.36	21.39	34.77	62.02	
7	21.39	23.88	34.80	61.85	
	Calculated for 2KCl.HgCl ₂ .H ₂ O,				4.11
8	20.32	27.62	..	65.24	2KCl.HgCl ₂ .H ₂ O and KCl.HgCl ₂ .H ₂ O
9	20.26	27.38	..	73.98	
10	17.85	25.34	21.89	75.10	KCl.HgCl ₂ .H ₂ O
11	9.26	18.95	21.02	73.36	
12	7.80	19.56	20.76	73.06	
13	6.84	22.81	20.75	74.54	
14	6.66	24.32	20.54	73.99	
	Calculated for KCl.HgCl ₂ .H ₂ O,				4.95
15	6.52	25.13	..	76.46	KCl.HgCl ₂ .H ₂ O and KCl.2HgCl ₂ .2H ₂ O
16	6.64	25.16	..	80.60	
17	6.27	25.11	12.09	83.20	KCl.2HgCl ₂ .2H ₂ O
18	5.77	24.73	11.87	83.18	
	Calculated for KCl.2HgCl ₂ .2H ₂ O,				5.52
19	4.68	24.75	..	84.46	KCl.2HgCl ₂ .2H ₂ O and HgCl ₂ HgCl ₂
20	4.66	25.17	..	93.68	
21	4.69	24.82	..	98.50	
22	none	6.90	none	100.00	

Table II.—Solubility of Sodium and Mercuric Chlorides at 25°.

No.	Per cent NaCl in solution.	Per cent HgCl ₂ in solution.	Per cent NaCl in residue.	Per cent HgCl ₂ in residue.	Per cent H ₂ O in residue.	Residue contains :
0	26.50	none	100.00	none		NaCl
1	18.66	51.35	. .	16.36	. .	NaCl and NaCl.HgCl ₂ .2H ₂ O
2	18.71	51.32	. .	21.98	. .	
3	18.64	51.42	. .	65.42	. .	
4	18.87	51.26	. .	71.25	. .	
5	14.97	57.74	16.38	74.18	9.44	NaCl.HgCl ₂ .2H ₂ O
6	14.03	59.69	16.36	74.21	9.43	
7	13.25	62.16	16.16	74.70	9.14	
8	13.17	62.59	15.96	74.76	9.28	
Calculated for NaCl.HgCl ₂ .2H ₂ O,						
			16.01	74.14	9.85	
9	12.97	62.50	. .	78.20	. .	NaCl.HgCl ₂ .2H ₂ O and HgCl ₂
10	13.14	62.48	. .	88.64	. .	
11	13.15	62.55	. .	90.83	. .	

It was thought possible that the 2 : 1 salt might form at a lower temperature and two solubility determinations were accordingly made at $10^{\circ}.3$. The mixtures were so chosen that, after saturation had taken place, the composition of the residues would correspond in one case to a mixture of sodium chloride and the 2 : 1 salt, and in the other to a mixture of the 2 : 1 and 1 : 1 compounds. The solubility apparatus was kept at $10^{\circ}.3$ by means of a cold water thermostat.¹ The results obtained were as follows :

Table III.—Solubility of Mixtures of Sodium and Mercuric Chlorides at $10^{\circ}.3$.

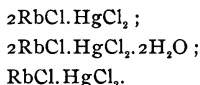
	Per cent NaCl in solution.	Per cent HgCl ₂ in solution.	Per cent NaCl in residue.	Per cent HgCl ₂ in residue.	Per cent H ₂ O in residue.
1	19.46	46.49	67.46	29.19	3.35
2	19.48	46.50	22.83	68.85	8.32
2NaCl.HgCl ₂ contains			30.16	69.84	none

The solubility is the same in the two experiments. The ratio of Na : Hg in the first residue is 10.7 : 1 and in the second 1.53 : 1. It follows that the same salts were present in both residues and that the 2 : 1 salt does not form. Had this salt formed, the solubility in the two experiments must have been different. It will be noticed, also, that both residues contain water of crystallization. We conclude from our results that the 2 : 1 salt which was described by Bonsdorf does not exist between $10^{\circ}.3$ and 25° and that he must have obtained mixtures of NaCl with the 1 : 1 salt.

RUBIDIUM MERCURIC CHLORIDES.

BY H. W. FOOTE AND L. H. LEVY.

Godeffroy described the following double rubidium mercuric chlorides :²



For our experiments pure rubidium chloride was obtained from rubidium alum which contained some potassium. It was

¹ Z. physik. Chem., 33, 749.

² Arch. der Pharm., [3], 12, 47.

partially separated from the potassium alum by repeated fractional crystallization and finally precipitated as Rb_2PbCl_6 . The spectroscope showed no trace of caesium or potassium. This work was done by one of us (Levy) under the direction of Professor H. L. Wells, to whom our thanks are due.

The solubility results obtained are given in Table IV. As before, constant residues showing double salts are italicized.

From the constant residues in the above table it will be seen that, at 25° , there exist 5 double rubidium-mercury chlorides with the following formulas :

- (1) $\text{RbCl} \cdot 5\text{HgCl}_2$;
- (2) $3\text{RbCl} \cdot 4\text{HgCl}_2 \cdot \text{H}_2\text{O}$;
- (3) $\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$;
- (4) $3\text{RbCl} \cdot 2\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$;
- (5) $2\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$.

None of these have the composition given by Godeffroy, although the double salt $2\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ lies between Godeffroy's double salts, $2\text{RbCl} \cdot \text{HgCl}_2$ and $2\text{RbCl} \cdot \text{HgCl}_2 \cdot 2\text{H}_2\text{O}$. That the double salt $2\text{RbCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ is stable at ordinary temperatures was shown when crystals, which had separated from a solution containing unknown amounts of rubidium and mercuric chlorides, were analyzed .

	RbCl.	HgCl ₂ .	H ₂ O.
I.	45.65	51.10	3.25
II.	45.25	51.18	3.57
Calculated for $2\text{RbCl} \cdot$ $\text{HgCl}_2 \cdot \text{H}_2\text{O}$,	45.55	51.05	3.40

These crystals were large and well defined.

The double salt $3\text{RbCl} \cdot 4\text{HgCl}_2 \cdot \text{H}_2\text{O}$ is an unusual type of an alkali halide double salt. To verify its existence, some of it was allowed to crystallize slowly in the thermostat at 25° , the crystals were separated from the mother liquor and dried in a room heated to 25° . Analysis :

	RbCl.	HgCl ₂ .	H ₂ O.
Found	25.32	73.39	1.29
Calculated for $3\text{RbCl} \cdot 4\text{HgCl}_2 \cdot$ H_2O	24.76	74.01	1.23

Table IV.—*Solubility of Rubidium and Mercuric Chlorides at 25°.*

No.	Per cent RbCl in solution.	Per cent HgCl ₂ in solution.	Per cent RbCl in residue.	Per cent HgCl ₂ in residue.	Per cent H ₂ O in residue.	Residue contains :
0	48.57	none	100.00	none	none	RbCl
1	46.76	9.18	88.04	11.24	0.72	RbCl and 2RbCl.HgCl ₂ .H ₂ O
2	47.54	9.49	60.33	37.51	2.16	
3	47.55	9.38	56.59	40.75	2.66	
4	47.30	9.47	46.73	49.38	3.89	
5	47.65	10.35	46.50	50.92	2.58	2RbCl.HgCl ₂ .H ₂ O
6	35.16	19.58	45.98	50.80	3.22	
Calculated for 2RbCl.HgCl ₂ .H ₂ O,						
7	34.77	19.94	43.07	52.44	4.49	2RbCl.HgCl ₂ .H ₂ O and 3RbCl.2HgCl ₂ .2H ₂ O
8	34.76	20.10	41.10	55.36	3.54	
9	30.27	20.17	39.07	57.34	3.59	3RbCl.2HgCl ₂ .2H ₂ O
10	29.20	20.55	39.10	57.47	3.43	
11	27.38	20.63	38.67	57.40	3.93	
Calculated for 3RbCl.2HgCl ₂ .2H ₂ O,						
12	26.83	20.87	38.48	57.36	3.82	3RbCl.2HgCl ₂ .2H ₂ O and RbCl.HgCl ₂ .H ₂ O
13	27.09	20.97	31.40	64.35	4.16	
14	26.15	20.58	30.34	65.48	4.18	RbCl.HgCl ₂ .H ₂ O
15	23.81	18.70	30.87	65.10	4.03	
16	18.10	14.25	29.87	65.28	4.85	
17	10.87	10.42	29.33	66.15	4.52	
Calculated for RbCl.HgCl ₂ .H ₂ O,						
			29.49	66.11	4.40	

Table IV.—*Solubility of Rubidium and Mercuric Chlorides at 25° (Continued).*

No.	Per cent RbCl in solution.	Per cent HgCl ₂ in solution.	Per cent RbCl in residue.	Per cent HgCl ₂ in residue.	Per cent H ₂ O in residue.	Residue contains :
18	10.68	10.56	28.59	67.99	3.42	RbCl.HgCl ₂ .H ₂ O and 3RbCl.4HgCl ₂ .H ₂ O
19	10.50	10.05	26.22	72.20	1.58	
20	10.06	9.86	25.28	73.38	0.84	3RbCl.4HgCl ₂ .H ₂ O
21	8.48	8.71	25.30	73.15	1.55	
22	8.46	8.80	25.44	73.67	0.89	
23	5.68	8.70	25.09	73.46	1.45	
24	5.10	8.33	24.92	73.93	1.15	
Calculated for 3RbCl.4HgCl ₂ .H ₂ O,						
25	3.43	8.25	22.79	75.72	1.49	3RbCl.4HgCl ₂ .H ₂ O and RbCl.5HgCl ₂
26	3.38	8.00	12.68	86.74	0.58	
27	2.98	7.71	8.40	91.24	..	RbCl.5HgCl ₂
28	1.89	7.64	8.38	91.78	..	
29	1.50	7.55	8.30	91.81	..	
30	1.10	7.21	8.07	91.58	..	
Calculated for RbCl.5HgCl ₂ ,						
31	0.79	7.16	6.91	93.15	..	RbCl.5HgCl ₂ and HgCl ₂ HgCl ₂
32	0.84	7.42	2.27	97.09	..	
33	none	6.90	none	100.00	..	

The crystals of this double salt separate in a mass of silky needles, difficult to free completely from the mother liquor.

The results of Table IV. are plotted graphically in Fig. I.,

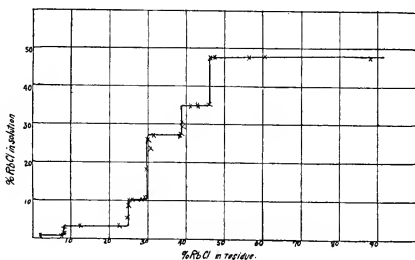


Fig. I.

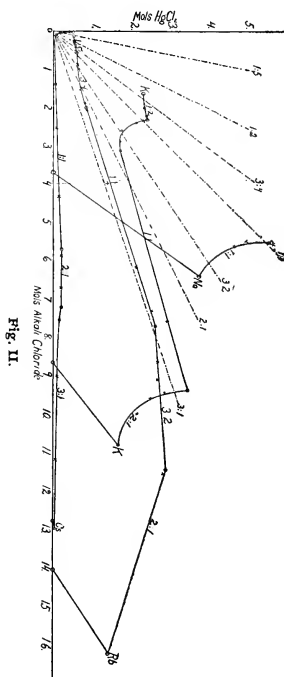
the abscissa representing the percentage of rubidium chloride in the residue, and the ordinate, the percentage of the same salt in solution. The vertical lines then show constant residue and variable solubility, corresponding to pure double salt, and the horizontal lines variable residue and constant solubility, corresponding to a mixture.

It seemed of interest to compare the solubilities of the salts of the different alkali metals. For this purpose the percentage composition of the solutions was recalculated to give the molecules of mercuric chloride and of alkali chloride dissolved in 100 molecules of water. The values for the caesium mercuric chlorides previously published¹ were also recalculated. The results obtained are plotted in the diagram, Fig. II. The molecules of mercuric chloride and of alkali chloride dissolved in 100 molecules of water are plotted, respectively, as ordinate and abscissa, except in the case of sodium chloride. Here the solubility was so great that the values obtained were multiplied by one-third. Each curve is designated by the symbol of the alkali metal present. The points on the curve where two salts were present together are represented by circles; by crosses where only one salt formed.

The dotted lines radiating from the intersection of the ordi-

¹ *Loc. cit.*

nate and abscissa represent the composition of solutions formed by dissolving the different double salts in water, and the behavior of a given double salt, on recrystallizing at 25° , is deter-



mined from the intersection of the dotted line representing its solutions with the solubility curve.¹ For instance, the composition of a solution of 1 : 1 salt is represented by some point on the dotted line, making an angle of 45° with the abscissa. This line cuts the solubility curve of the 1 : 1 salts of sodium,

¹ Van't Hoff : Vorles. über Bild. und Spalt. von Doppelsalzen.

potassium and caesium and the curve of the 3 : 4 salt of rubidium, showing that these salts can be in equilibrium with a solution containing equal molecules of the alkali chloride and mercuric chloride. The 1 : 1 salts of sodium, potassium and caesium can, therefore, be recrystallized, while the rubidium salt first yields the 3 : 4 compound.

The behavior of the various salts, on recrystallizing, is as follows :

3 : 1.—Only the caesium salt forms. On recrystallizing, it yields the 1 : 1 type.

2 : 1.—The potassium and caesium salts yield the 1 : 1 type. The rubidium salt forms the 3 : 4.

3 : 2.—Only the rubidium salt forms. On recrystallizing it yields the 3 : 4.

1 : 1.—The sodium, potassium and caesium salts recrystallize. The rubidium salt yields the 3 : 4.

3 : 4.—Only the rubidium salt forms. It yields the 1 : 5.

1 : 2.—The potassium salt yields mercuric chloride ; the caesium salt the 1 : 1.

1 : 5.—The rubidium salt yields mercuric chloride ; the caesium salt the 1 : 2.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
November, 1905.

Contribution from the Chemical Laboratories of Harvard University.
ON THE ADDITION PRODUCTS OF *p*-NITROSODIMETHYLANILINE WITH CERTAIN PHENOLS.

BY HENRY A. TORREY AND J. A. GIBSON.

In an earlier paper by H. Hardenbergh and one of us¹ it was shown that quinhydrone and phenoquinone were addition products which, on solution in benzene and other neutral solvents, were dissociated into their constituent parts, namely, quinone and hydroquinone in the former and quinone and phenol in the latter case. Paranitrosodimethylaniline, which is frequently given the quinoid structure, seems to form similar compounds with certain substituted phenols. Edeleanu

¹ THIS JOURNAL, 33, 167.

and Euescu¹ have described a few bodies of this nature and we have somewhat extended the number. We have found that there is a considerable degree of analogy between phenoquinone and quinhydrone and the products from *p*-nitrosodimethylaniline. Quinone unites with 2 molecules of a monatomic phenol and 1 molecule of a diatomic, and we find this also to be true, for the most part, of *p*-nitrosodimethylaniline. Further, the compounds of the latter with 2 molecules of the phenol, in the solid state, resemble phenoquinone in color, whereas those with 1 molecule of the diatomic phenol are more nearly like quinhydrone, and just as phenoquinone and quinhydrone both dissolve with the yellow color of quinone, these derivatives of *p*-nitrosodimethylaniline dissolve with the green color of the latter body. That this is due to the dissociation of these addition products into the phenol and *p*-nitrosodimethylaniline is shown by the molecular weight determinations given below.

We shall consider first the products from monatomic phenols and then those from polyatomic phenols.

Trichlorphenol and p-Nitrosodimethylaniline.

One gram of *p*-nitrosodimethylaniline was dissolved in a very small quantity of warm benzene and was added to a concentrated benzene solution of 2 grams of trichlorphenol. No precipitation occurred immediately, but on adding ligroin the crystallization began and, after the mixture had stood for a short time, a good yield of fine, reddish crystals of the product described by Edeleanu and Euescu was obtained.² The product was filtered, washed with ligroin and dried in a vacuum desiccator; it melted at 91°. That the trichlorphenol used in the preparation was pure was shown by the melting-point, 67°, and an analysis. Cl required 53.92, found 53.88 per cent.

An analysis of the product of the reaction shows the percentage of chlorine required by an addition product formed from 2 molecules of trichlorphenol and 1 molecule of *p*-nitrosodimethylaniline, $\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot (\text{C}_6\text{H}_2\text{Cl}_3\text{OH})_2$.

¹ J. Chem. Soc., 70, 1, 359 (1896).

² *Loc. cit.*

0.2282 gram substance gave, by the sodium peroxide method,¹ 0.3582 gram AgCl.

	Calculated for $\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot (\text{C}_6\text{H}_2\text{Cl}_3\text{OH})_2$.	Found.
Cl	39.08	38.84

The body which, in the solid condition, consisted of fine, deep red crystals, dissolved in all solvents with the characteristic green color of *p*-nitrosodimethylaniline. Its solubility is as follows: Readily soluble in cold chloroform, alcohol, acetone and benzene; soluble in ether; insoluble in cold ligroin, but slightly soluble in the hot liquid.

The following molecular weight determination shows that the addition product is completely dissociated in these solvents into *p*-nitrosodimethylaniline and trichlorphenol, and that the green color is due to the free *p*-nitrosodimethylaniline, since the trichlorphenol, of course, is colorless.

The molecular weights are calculated from the well known formula $M = \frac{100 K s}{W x}$.

In the tables the concentration is given in grams of dissolved substance in 100 grams of the solvent.

Molecular Weight of Addition Product of Trichlorphenol and of p-Nitrosodimethylaniline by the Ebullioscopic Method.

W.	s.	x.	K.	M.
100	0.5830	0.087	26.7	178
.	1.3701	0.197	.	186
.	2.0054	0.284	.	184
.	2.6837	0.401	.	179

The molecular weight is found to be one-third of the molecular weight of $\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot (\text{C}_6\text{H}_2\text{Cl}_3\text{OH})_2$, $\frac{543}{3} = 178$; this is as it should be if the dissociation is complete.

Tribromphenol and p-Nitrosodimethylaniline.

This addition product was made in a similar manner to that used for the trichlorphenol derivative, by adding 1 gram of the *p*-nitrosodimethylaniline, dissolved in 5 cc. of benzene, to 5

¹ Pringsheim: THIS JOURNAL, 31, 386.

grams of tribromphenol in 10 cc. of benzene. After standing some time, dark red crystals with a blue reflex separated in large quantities. These were collected on a filter, washed with ligroin and, after drying, were analyzed :

0.2250 gram substance gave, by the sodium peroxide method, 0.3114 gram AgBr.

Br	Calculated for	Found.
	$\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot (\text{C}_6\text{H}_2\text{Br}_3\text{OH})_2$	
	59.11	58.90

The analysis shows that the substance was pure.¹ The following molecular weight determination proves that the addition product is completely dissociated when dissolved in benzene.

Molecular Weight of Addition Product of Tribromphenol and p-Nitrosodimethylaniline by the Ebullioscopic Method.

W.	s.	x.	K.	M.
100	1.5740	0.160	26.7	262
.	3.7248	0.362	.	274
.	6.4259	0.590	.	290
.	8.0906	0.732	.	295
.	9.2783	0.834	.	297

Its solubilities are practically the same as those of the trichlorophenol derivative and in all cases its solutions are green.

The Addition Product of Salicylic Acid and p-Nitrosodimethylaniline.

When 2 grams of *p*-nitrosodimethylaniline, dissolved in 15 cc. of benzene, are added to 4 grams of salicylic acid, dissolved in 50 cc. of benzene, a deep orange-red, crystalline precipitate falls. This was collected on a filter, dried on a clay plate and afterwards in a vacuum desiccator. The yield of the dry substance was very good. Recrystallized from hot benzene, it gives fine, dark red needles, melting at 110°.

I. 0.2251 gram substance gave 13.9 cc. moist N at 27°.3 and 765 mm.

II. 0.4540 gram substance gave 27.1 cc. moist N at 23° and 759.5 mm.

¹ The tribromphenol used in making this preparation was also analyzed for bromine. Found, 72.48; required, 72.51 per cent.

	Calculated for		Found.	
	$\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot (\text{HOC}_6\text{H}_4\text{COOH})_2$		I.	II.
N	6.57		6.85	6.72

The analysis and the color of the compound indicate that it is an addition product similar to those formed by the other two phenols investigated. It cannot be a *salt* of *p*-nitrosodimethylaniline, for the latter would unite with only one equivalent of the acid and, further, the product dissolves in organic solvents, such as benzene, with a green color. Were it a salt it would, in all probability, be insoluble in benzene.

The Addition Products of p-Nitrosodimethylaniline with Diatomic Phenols.

These bodies divide themselves into two classes, those in which 1 molecule of the *p*-nitrosodimethylaniline unites with 1 molecule of the phenol, as was the case with trichlorresorcinol, and which reminds one of quinhydrone, which is made up of a molecule each of quinone and hydroquinone, and those in which the 2 molecules of the base unite with 1 molecule of the phenol, as was the case with tribromresorcinol and pyrocatechol.

Addition Product of p-Nitrosodimethylaniline and Trichlorresorcinol.

One gram of *p*-nitrosodimethylaniline, dissolved in benzene, was added to 1.5 grams of trichlorresorcinol in the same solvent. The product, which was also obtained by Edeleanu and Eulescu, was purified by recrystallization from hot benzene, which gave a substance consisting of dark blue crystals, which, however, when ground up were reddish brown. Determination of chlorine :

0.2104 gram substance gave 0.2462 gram AgCl.

	Calculated for $\text{ONC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_4\text{Cl}_3(\text{OH})_2$.	Found.
Cl	29.27	28.94

This body dissolves in organic solvents, such as benzene, ether, chloroform, alcohol and acetone with a green color, and a molecular weight determination in benzene shows it to be an addition product which is practically completely dissociated on

solution. The molecular weight of the completely dissociated compound should be $\frac{363.5}{2}$ or 181.8.

Molecular Weight of Addition Product of p-Nitrosodimethylaniline and Trichlorresorcinol by the Ebullioscopic Method.

W.	S.	X.	K.	M.
100	0.5598	0.074	26.7	202
.	1.0757	0.145	.	198
.	1.6319	0.220	.	198
.	2.3078	0.311	.	198

Addition Products of p-Nitrosodimethylaniline and Tribromresorcinol.

The product obtained by mixing benzene solutions of tribromresorcinol and *p*-nitrosodimethylaniline differs from that from trichlorresorcinol in that it contains 2 molecules of the base to 1 of the phenol. The result is the same whether 1 molecule of the tribromresorcinol is mixed with 2 molecules of the aniline or with only 1 molecule. The product separates out in the form of light, olive-green crystals, which may be purified by crystallization from hot benzene. It melts at 115°.

The tribromresorcinol used in the preparation was analyzed and found to be pure.

The bromine determinations in the addition product gave the following results:

- I. 0.1748 gram substance gave 0.1516 gram AgBr.
- II. 0.1904 gram substance gave 0.1645 gram AgBr.

Calculated for [ONC ₆ H ₄ N(CH ₃) ₂] ₂ .C ₆ HBr ₃ (OH) ₂ .		Found.	
Br		I.	II.
	37.09	36.91	36.76

It is easily soluble in benzene, chloroform, acetone; also soluble in alcohol and ether; nearly insoluble in ligroin.

All of its solutions are *green*.

Addition Product of p-Nitrosodimethylaniline and Pyrocatechol.

Like tribromresorcinol, pyrocatechol gives a product in which 2 molecules of the base are united with 1 molecule of the phenol. Two grams of *p*-nitrosodimethylaniline, dissolved in 25 cc. of warm benzene, were added to 1.5 grams pyrocate-

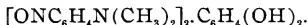
chol in 50 cc. of benzene. An abundant yield of fine, olive-green crystals was obtained. The body, after recrystallization from hot benzene, melts, with decomposition, at 125°.

I. 0.3023 gram substance gave 36 cc. N at 18°.5 and 760.6 mm.

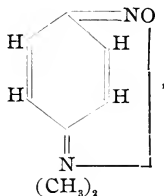
II. 0.3052 gram substance gave 37.9 cc. N at 23°.6 and 756.4 mm.

Calculated for [ONC ₆ H ₄ N(CH ₃) ₂] ₂ .C ₆ H ₄ (OH) ₂ .		Found.	
		I.	II.
N	13.66	13.73	13.88

The body is evidently an addition product composed of 2 molecules of the aniline and 1 of the phenol,



It dissolves in organic solvents with a green color. These addition products of *p*-nitrosodimethylaniline with mono- and di-atomic phenols exhibit a rather striking analogy to the phenoquinone and quinhydrone, which have also been shown¹ to be addition products that completely dissociate in organic solvents. Paranitrosodimethylaniline is frequently given the quinone formula,

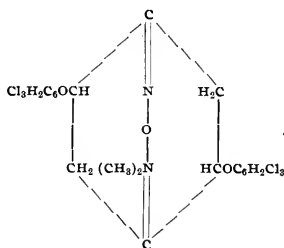


and inasmuch as Posner² has shown that in phenoquinone and similar compounds the point of addition of phenol is probably at the double bonds, and since this constitution is in harmony with the dissociation of these compounds, we are justified in suggesting that these addition products of *p*-nitrosodimethylaniline are of a similar nature. The analogy is further supported by the fact that *p*-nitrosodimethylaniline unites with 2

¹ THIS JOURNAL, 22, 167. Beltris Acad. Roy. d. Belgique, [iii], 32, 300; 35, 60.

² Ann. Chem. (Liebig), 336, 85.

molecules of a monatomic phenol, just as quinone does, whereas with a diatomic it unites with only 1 molecule (cf. quinhydrone), or 2 molecules of the aniline unite with 1 of the diatomic phenol. For example, the constitution of the addition product with trichlorophenol would be :



The constitution of the other addition product would be formulated in a similar manner.

Attempts to obtain corresponding compounds with pyrogalllic acid and tetrachlorpyrocatechol were unsuccessful, instead of the addition products being readily soluble in organic solvents, dark brown or black substances were obtained, difficultly soluble and not giving in solution the characteristic bright green color of *p*-nitrosodimethylaniline.

The work described in this paper was done in the chemical laboratory of Radcliffe College.

VARIABLE SENSITIVENESS IN THE COLORIMETRY OF CHROMIUM.

BY D. W. HORN.

It is either stated or implied in the descriptions of colorimetric methods that they are to be applied to dilute solutions.

This practice seems to have originated in the observation that the results of parallel determinations made in deeply colored (not very dilute) solutions do not approximate sufficiently to the average value. In some instances, as in the use of "Nessler's Reagent," there is a different color characterizing solutions that are recognized as too concentrated, but such instances are exceptional. In cases where alteration in concentration is not accompanied by any change in color, but only by a variation in the depth of the color, it has been, hitherto, merely a matter of individual judgment as to what shades are best adapted to the purposes of quantitative analysis.

The application of colorimetric methods in this general way involves one assumption at least, namely, that any given method is practically of equal sensitiveness in all solutions more dilute than those that are unmistakably too deeply colored for use. If, for convenience, we define as the sensitiveness of a colorimetric method the reciprocal of the weight in milligrams of the colored solute that produces that change in color that can just be differentiated with certainty, the assumption referred to is that the variations in the sensitiveness of any method are negligible.

Being about to make some colorimetric measurements, it occurred to me that this assumption was without experimental verification. It is evident that, if the sensitiveness of a colorimetric method should prove experimentally to be a variable, there must be for that method a set of definite conditions under which the sensitiveness will have a maximum value. Further, unless these conditions for maximum sensitiveness are determined experimentally for each of the colorimetric methods used for the accurate quantitative estimation of minute amounts of substances, the corresponding methods cannot be used with any assurance of maximum accuracy or with maximum ease in making the comparisons.

The results of an examination of the sensitiveness of the colorimetric estimation of chromium are presented in this paper. As similar results have been obtained by several observers in this laboratory, I am of the opinion that the effect of the personal equation on the general facts is negligible. The

results show that the sensitiveness is beyond a doubt variable, and that the *ease* of determination varies also with the concentration. The latter is measured, roughly, by the variation from the mean when the same two concentrations are compared without and with intermediate shades to aid in the comparison. The general relation between sensitiveness and concentration is not a simple one, nor such as would be likely to be predicted.

In the first column in the following table of results,¹ the concentrations at which comparisons were made are given in terms of the number of liters of solution containing 1 gram-atom of chromium; in the second, the weights of chromium in grams that could just be differentiated with certainty when present in 50 cc. of solution; in the third, the weights of potassium chromate in milligrams that could just be differentiated with certainty when present in 50 cc. of solution; in the fourth, the values for the sensitiveness; and in the fifth, the variation from the mean in grams of chromium shown by the values obtained when the comparisons were made with and without a number of solutions of concentrations and colors of nearly the same value, to aid in the differentiation from each other of the two most nearly alike:

I. Liters.	II. Grams.	III. Milligrams.	IV. Sensitiveness.	V. Grams.
250.0	0.003979	14.81	0.07	0.000500
500.0	0.000784	2.92	0.34	0.000048
666.6	0.000386	1.44	0.69	0.000050
1000.0	0.000184	0.69	1.45	0.000037
2000.0	0.000074	0.28	3.59	0.000000
3600.0	0.000007	0.03	33.33	
4000.0	0.000002	0.01	100.00	0.000000
7500.0	0.000003	0.01	100.00	
8000.0	0.000001	0.004	250.00	0.000000
9900.0	0.000005	0.02	50.00	
10666.6	0.000008	0.03	33.33	0.000001
16000.0	0.000011	0.04	25.00	0.000002
17700.0	0.000003	0.01	100.00	
32000.0	0.0000007	0.003	333.33	0.0000002
110000.0	0.000011	0.04	25.00	
150000.0	0.000008	0.03	33.33	
200000.0 not distinguishable from distilled water.				

¹ I am indebted to E. F. Bliss, M. D. Eby, A. I. Jonas, F. C. Child and A. Ross for many of the measurements made in connection with this subject.

In this case the sensitiveness had a maximum value at concentrations between 0.004 N and 0.008 N, with respect to the gram-atom of chromium. The ease with which the comparisons were made was also at a maximum at these concentrations, for complete agreement existed between the results obtained under the two sets of conditions already mentioned.

A rather anomalous fact appeared after the minimum amount of chromium that had to be present in the distilled water to give it a detectable color was determined. The minimum quantity required was 0.000013 gram of chromium, whereas 0.000001 gram produced a readily detectable difference in the depth of color at the concentrations of maximum sensitiveness. In other words, it was easier, by far, to tell the difference between two colored liquids than between a colored and a colorless one.

Some measurements of the sensitiveness of the colorimetry of chromium in solutions of green chromium chloride were also made. The results appear in the following table in columns corresponding to those in the previous table :

I.	II.	III.	IV.	V.
Liters.	Grams.	Milligrams.	Sensitiveness.	Grams.
1000	0.000156	0.474	2.11	
1550	0.000084	0.255	3.92	
3000	0.000021	0.064	15.63	
9700	0.000268	0.815	1.23	

The decrease in sensitiveness at the last concentration given was probably due to precipitated chromium hydroxide resulting from the hydrolysis of the chloride. It is generally recognized that colorimetric comparisons cannot be made readily in turbid liquids. So far as determined, however, the general behavior of the sensitiveness is the same as in yellow chromium solutions.

Details of Experimental Work.

The comparisons were made in Nessler cylinders of 50 cc. capacity, with flat bottoms and of approximately the same internal diameter. The depth of colored liquid varied between 10 and 10.2 cm. Each cylinder was jacketed in black paper, such as is used in packing photographic plates. An efficient

form of stirring rod was used to insure uniformity in the liquids that were to be compared.

The solutions were measured from burettes of 50, 25, 10, or 2 cc. capacity, as best suited the volume that had to be measured. These, and the measuring flasks used, had been calibrated previously, though the corrections thus introduced proved, in the course of the work, to be negligible.

The comparisons were made in daylight reflected from a white porcelain surface, usually placed about a meter away from a north window. They were made at any hour of the day that was convenient, and on cloudy as well as on clear days.

The solutions were made from potassium bichromate that had been recrystallized 7 times from distilled water. Shortly before use it was fused in porcelain, broken up quickly in an agate mortar, and subsequently kept in a desiccator over concentrated sulphuric acid. Potassium hydroxide (Kahlbaum) was used in the solutions of the chromate in the proportion of 2 mol. to 1 of $K_2Cr_2O_7$. The green solutions were made by reducing the bichromate with alcohol and a small amount of hydrochloric acid; the greater part of the excess of alcohol and acid was driven off by evaporation on a water-bath before the solution was diluted.

The water used was the ordinary distilled water of the laboratory.

Two methods of comparison were employed, the one was that usually followed in colorimetric work—the method of approximation. When two concentrations were found that could not be distinguished from each other, a third was prepared slightly stronger than the stronger of the first two. When such a third solution was found that could be differentiated from the weakest, at least 5 times in 7 trials, the difference was recorded as just capable of being differentiated.

Several days later 2 solutions of concentrations that had previously been found to be just capable of differentiation were presented to the same observer. If the difference was not recognized another pair of tubes, differing somewhat more in concentration, was presented, and so on as long as necessary

for the establishment of a new limit for the difference in depth of color just distinguishable.

In all these cases the solutions were prepared and the tubes thoroughly mixed each time by some one who was not making the comparisons. The distinguishing marks on the cylinders were known only to this person, who also made a record of the result of each comparison, without telling the observer of the outcome of any one of them until all 7 had been made and recorded.

The other plan involved the preparation of a series of 7 or more solutions in which, beginning with the most dilute, there was a small but constant increment in the amount of colored solute present. When the members of this series included two that could be differentiated, it was comparatively easy to tell directly, by comparing several or all of them, just what difference in color was distinguishable and to just what amount of solute it corresponded. By selecting the concentrations properly and by having a sufficient number of tubes in the series, it was possible to arrive at the same result a number of times with different cylinders.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1905.

CINNAMYLDENEACETIC ACID AND SOME OF ITS TRANSFORMATION PRODUCTS.

BY ARTHUR MICHAEL AND WIGHTMAN W. GARNER.

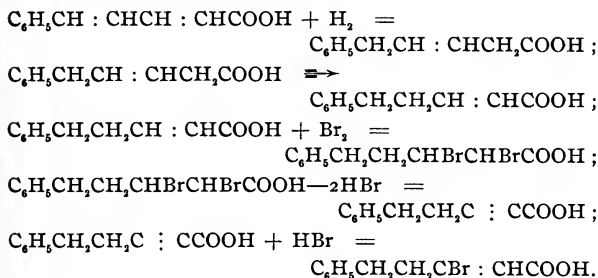
This work was originally taken up with a view to determine whether any evidence could be obtained bearing on the existence of more than two stereomeric forms in the homologues of cinnamic acid. δ -Phenyl- Δ^{α} -pentenoic acid,



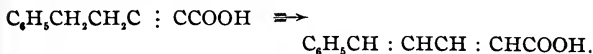
was selected for the purpose as being the substance most readily obtained, and it was proposed to carry out the investigation along the same lines that have been applied to the cinnamic acids. It has been shown that when β -allobromcinnamic acid (159°) is reduced with zinc dust and alcohol there is obtained,

in addition to allo- and cinnamic acids,¹ a lower melting product which, at the time this investigation was carried out, was regarded as a third isomeric acid.²

The cinnamylideneacetic acid was converted, by nascent hydrogen, into δ -phenyl- Δ^{β} -pentenoic acid and the latter transformed, by boiling with sodium hydroxide solution, into the Δ^{α} -acid. The dibromide of the Δ^{α} -pentenoic acid was then prepared by the addition of bromine, in chloroform solution. It was thought that a derivative of propiolic acid could be obtained from this dibromide by means of alcoholic potassium hydroxide, which, by the addition of hydrobromic acid, should give β -brom- Δ^{α} -phenylpentenoic acid. These changes may be represented by the following equations :



However, on treating the Δ^{α} -pentenoic acid dibromide with alcoholic potassium hydroxide in excess, the original product, cinnamylideneacetic acid, was obtained and not a propiolic derivative. It appears, therefore, that the latter is unstable in the presence of alkali and, if formed at all, passes at once into the isomeric form :

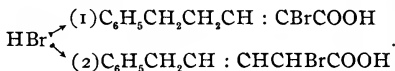


The question then arises, whether the rearrangement takes place with the removal of the first molecule of hydrobromic acid, or by the action of potassium hydroxide on the propiolic

¹ Liebermann : Ber. d. chem. Ges., **25**, 950.

² Michael and Whitehorn : *Ibid.*, **34**, 3647.

derivative? The problem is complicated by the fact that elimination of hydrobromic acid from the dibromide may occur in several different ways. Assuming that the β -bromine atom is first removed, the reaction may proceed in two directions :



Moreover, each of these acids can exist in two stereomeric forms. That a mixture of structurally different monobrom acids may be formed is indicated by the experiments of Fittig,¹ who showed that boiling β -monobrom derivatives of normal fatty acids with water leads to the formation of some Δ^β -acids, although in considerably less proportion than the Δ^α -derivatives. When the above acid dibromide is treated with alcoholic potassium hydroxide, in the proportion of 1 molecule of acid to 2 of the alkali, a product is obtained consisting of at least two isomeric monobrom acids. These acids do not appear to be stereomeric, for they are stable towards heat and can be esterified without change ; if they should be stereomeric, at least they differ in their behavior from any similar acids as yet known.

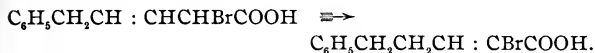
A discussion of the changes that may occur when α -brom- Δ^β -phenylpentenoic acid (2) is boiled with alkali is more suggestive of possibilities than of probabilities, as, theoretically, the subject is exceedingly complicated and the experimental basis for such speculations is extremely limited.² Fittig³ has, indeed, demonstrated that such Δ^β -alkenoic acids, whose γ -carbon is joined to alkyl or benzyl, when boiled with alkali are mainly converted into the Δ^α -isomers, but the process is never complete, as the latter acids go over, by addition of water, into the β -hydroxyalkanoic acids and these are partially converted into the original Δ^β -acids. If, however, phenyl replaces alkyl or benzyl, for instance with γ -phenyl- Δ^β -butenoic acid,

¹ Ann. Chem. (Liebig), 283, 61.

² The recent investigation of Riiber (Ber. d. chem. Ges., 38, 2742) shows how complicated the ultramolecular changes are in this series;

³ Ann. Chem. (Liebig), 283, 61.

only traces of the acid undergo such a rearrangement. If an intramolecular rearrangement of unsaturation in the above monobrom acid precedes the elimination of hydrobromic acid, then, by analogy with the mother acid, the following change would take place :



In order to obtain some experimental evidence on this point a number of aromatic acids were oxidized with potassium permanganate under different conditions. Those acids of the general type $\text{C}_6\text{H}_5\text{CH} : \text{C(R)COOH}$ invariably give benzaldehyde when oxidized in the presence of dilute sodium carbonate or strong potassium hydroxide. Phenylacetic acid gives benzaldehyde when dissolved in sodium carbonate, but does not give the aldehyde in the presence of much free alkali. Hydrocinnamic acid gives no aldehyde in either case. Δ^{α} -Phenylpentenoic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH} : \text{CHCOOH}$, in the presence of free alkali, gives a small amount of benzaldehyde, but when the free acid is oxidized no aldehyde is obtained. The difference in conduct towards potassium permanganate between the last-mentioned acid and hydrocinnamic acid may, however, be due to the action of the alkali on the former, converting it, partially, into the Δ^{β} -acid, which gives the aldehyde on oxidation.

The mixture of monobrom acids obtained by the action of alcoholic potassium hydroxide on the phenyl- α,β -dibrompentenoic acid gives, on oxidation, in neutral solution, as well as when dissolved in sodium carbonate and in the presence of free alkali, small amounts of benzaldehyde. This fact seems to indicate that in the mixture of monobrom acids at least a part of the product has gone over into an acid whose unsaturated carbons are nearer to the phenyl than in a Δ^{α} -acid and that the formation of cinnamylideneacetic acid results without the previous formation of a propiolic derivative. Again, when the mixture of monobrom acids is boiled several hours, with a large excess of alcoholic potassium hydroxide, only a small yield of cinnamylideneacetic acid is obtained, not more than

10-20 per cent. By repeating the operation, a second quantity, approximately equal to the first, is obtained and, after the removal of this, the residue, consisting of the greater portion of the whole, still contains halogen. If this residue is esterified and the ester distilled *in vacuo*, hydrobromic acid is evolved and, after saponification with alcoholic potassium hydroxide, a small quantity of cinnamylideneacetic acid is again obtained. The residue, however, still contains bromine. It is evident, therefore, that the second atom of bromine is removed with very great difficulty from the dibromide, and further, that whatever the constitution of the intermediate products, the final result is always of the nature of an acrylic and not a propiolic derivative. This behavior appears to indicate a shifting of the position of the unsaturation before the elimination of hydrobromic acid occurs and that this rearrangement is in a reversible condition, as is the case in the experiments described by Fittig. This would explain why only a part of the monobrom acids is converted by each treatment with alkali. Although it cannot be said with certainty whether the rearrangement of the unsaturation takes place before or after the removal of the second bromine atom, the above results favor the former possibility.

Preparation of α,β -Dibrom- δ -phenylpentenoic Acid.

Cinnamylideneacetic acid, which forms the starting point in the preparation of the above-mentioned acid, was first made by Perkin, Sr.,¹ from cinnamic aldehyde and potassium acetate; later by Fittig and Mayer,² who modified the method of Perkin. Our material was obtained according to the directions of Fittig and Mayer, with some minor modifications. It was found that nearly all of the reaction product goes into solution when boiled with a large quantity of *dilute* sodium carbonate, whereas it is very difficultly soluble in strong alkali. A small amount of a tarry substance is dissolved along with the acid, but this can be removed by fractional precipitation with hydrochloric acid. The latter is carefully added until the precipitate begins to come down colorless and the solution is then fil-

¹ J. Chem. Soc., 31, 403.

² Ann. Chem. (Liebig), 268, 50.

tered. From the filtrate the acid can be precipitated in almost pure condition. The yield obtained is 30-35 per cent of the weight of the aldehyde used. This product was next reduced with sodium amalgam, according to the directions of Fittig and Hofmann,¹ and the resulting δ -phenyl- Δ^8 -pentenoic acid boiled 10 hours with a 10 per cent aqueous solution of sodium hydroxide, containing 10 molecules of the latter to 1 of the acid.² After removal of the Δ^8 -pentenoic acid, formed by the action of the alkali, by crystallization from ether, the mother liquor was again treated with sodium hydroxide and, finally, the process repeated a third time. The total yield obtained is about 60 per cent of the theoretical quantity.

Fittig and Perrin³ prepared the dibromide of the Δ^8 -pentenoic acid by addition of bromine to the acid dissolved in a mixture of ether and carbon bisulphide. By this method the halogen adds with difficulty, and much hydrobromic acid is formed in spite of all precautions. Better results were obtained in the following way: The acid is suspended in 15-20 volumes of dry chloroform, in a ground glass-stoppered bottle, the calculated quantity of bromine is then added and the mixture allowed to stand at a low temperature, 4 or 5 days, in diffused light. The addition product obtained in this way is recrystallized from a hot mixture of 2 parts benzene and 1 part ligroin, and shows the properties of Fittig and Perrins' dibromide.

Action of Alcoholic Potassium Hydroxide on α,β -Dibrom- δ -phenylpentanoic Acid.

To a solution of 20 grams of the dibromide in alcohol, somewhat more than the calculated quantity (2 mols.) of alcoholic potassium hydroxide was slowly added. After the mixture had been allowed to stand for several hours, the alcohol was evaporated on the water-bath, the residue dissolved in water, the solution extracted with ether and then acidified. The liberated acids, which were precipitated as a heavy oil, were

¹ Ann. Chem. (Liebig), 283, 309.

² Riiber (Ber. d. chem. Ges., 38, 2747) has recently shown that some Δ^7 -acid is also formed in this operation.

³ Ann. Chem. (Liebig), 283, 326.

taken up with ether. After removal of the latter the residue was dissolved in hot chloroform and 2 volumes of ligroin added to the solution. On standing, clusters of fine needles separated which melted at 67° – 75° and were soluble in all ordinary media except ligroin. There were obtained 6 grams of this product. Repeated recrystallization from a mixture of chloroform and ligroin did not improve its melting point, which likewise remained unchanged after repeated fusion of the acid mixture. Analysis:

0.1542 gram substance gave 0.1151 gram AgBr.

	Calculated for $C_6H_5C_2H_4C_2HBrCOOH$.	Found.
Br	31.37	31.73

By spontaneous evaporation of the mother liquors a heavy oil, easily soluble in all the common organic solvents except ligroin, was precipitated. This oil contained bromine but could not be obtained in a solid form. A second portion of the dibromide was boiled 4 hours with an equal weight of potassium hydroxide dissolved in alcohol. A thick oil was obtained which contained bromine, but did not solidify on long standing. The treatment with alcoholic potassium hydroxide was variously modified as to time of boiling and quantity of alkali used, but all efforts to obtain a crystalline product in this way were unsuccessful.

An attempt was made to obtain better results through the ester dibromide. Twenty grams of the Δ^{β} -acid were esterified by treatment with sulphuric acid and alcohol, according to the Purdie method.¹ The ester was obtained as an oil boiling at 178° (25 mm.). This was dissolved in 2 volumes of carbon bisulphide and the calculated quantity (1 mol.) of bromine, in carbon bisulphide, slowly added. Addition took place very readily and without the formation of more than traces of hydrobromic acid. The ester dibromide was then treated with 2 molecules of alcoholic potassium hydroxide in the cold, but as the resulting product could not be brought to crystallize it was converted into the ethyl ester, which boiled at 178° – 184° (8–11 mm.) but with so considerable a decomposition that it was

not considered sufficiently pure for further experiments. Finally, 20 grams of the acid dibromide were converted into the mixture of monobrom acids by treatment with cold alcoholic potassium hydroxide, the product converted into the ethyl ester and this boiled 6 hours with 0.6 of its weight of potassium hydroxide, dissolved in 5 parts of alcohol. A thick oil was obtained which contained halogen. This was dissolved in hot, 60 per cent alcohol and, on standing, about 2 grams of a crystalline substance separated out which melted at 165° and showed the other properties of cinnamylideneacetic acid. The oil from the mother liquor was again treated with alcoholic potassium hydroxide in the same manner and about the same quantity of cinnamylideneacetic acid was again obtained. The residual oil, which still showed the presence of bromine, was esterified and the resulting ester distilled in a vacuum. In the first distillation a heavy oil went over at 180° – 195° (18 mm.) with evolution of much hydrobromic acid. This was again distilled and boiled at 180° – 185° (18 mm.). After saponifying with alcoholic potassium hydroxide and crystallizing from benzene, cinnamylideneacetic acid was once more obtained. Similar results were also observed by treating the dibromide directly with a large excess of alcoholic potassium hydroxide.

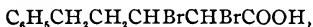
Oxidation of Some Aromatic Acids.

A dilute solution of potassium permanganate was allowed to drop slowly into a boiling solution of the acid to be oxidized and the resulting distillate examined for aldehyde. A simple and convenient form of apparatus for conducting the experiment consists of a distilling flask, the neck of which is fitted with a dropping funnel and the side tube connected with a condenser. Under these conditions the aldehyde formed in the first stages of the oxidation passes over at once, in part at least, and thus escapes the further action of the permanganate. The aldehydes were identified by precipitation as phenylhydrazones or as semicarbazones. Each of the acids examined was oxidized with the permanganate under different conditions, as follows: (1) In the free state; (2) dissolved in sodium carbonate; (3) in the presence of a large excess of free alkali.

Each of the acids of the cinnamic acid type was found to give benzaldehyde under all the above-mentioned conditions. The acids belonging to this group, which were examined, are cinnamic acid, α -bromcinnamic acid, α -ethylcinnamic acid and α -butylcinnamic acid. Phenylacetic acid, in dilute sodium carbonate solution, gives benzaldehyde, but in the presence of free alkali does not give the aldehyde. This behavior affords a means of detecting the cinnamic acid derivatives in the presence of phenylacetic acid.

Hydrocinnamic acid gives no aldehyde in sodium carbonate solution, which fact differentiates it from the cinnamic acid group; nor does it give any aldehyde in the presence of free alkali, in which respect it differs from phenylacetic acid. δ -Phenyl- Δ^a -pentenoic acid, $C_6H_5CH_2CH_2CH:CHCOOH$, gives benzaldehyde in the presence of free alkali, but when the free acid is oxidized no aldehyde is obtained.

The mixture of monobrom acids resulting from the action of alcoholic potash on the dibromide,



gives benzaldehyde when oxidized in the free state, as well as in the presence of carbonate and free alkali. The identity of the aldehyde was established by converting it into the phenylhydrazone, m. p. 152° , and also into the semicarbazone, m. p. 214° .

Hydrocinnamic Aldehyde.

Since the formation of this aldehyde was not excluded in some of the experiments described above, it was prepared according to directions of v. Miller and Rohde.¹ Hydrocinnamic aldehyde reacts with semicarbazine hydrochloride to form a semicarbazone, which crystallizes in colorless leaflets, easily soluble in alcohol, but difficultly soluble in water. It melts at 125° . Analysis:

0.1133 gram substance gave 21.7 cc. N at 21° and 767 mm.

¹ Ber. d. chem. Ges., 23, 1080.

	Calculated for $C_6H_5C_2H_4CHCH_3ON_3$.	Found.
N	21.98	22.02

TUFTS COLLEGE, MASS.

MAGNESIUM PERMANGANATE AS AN OXIDIZING AGENT.

BY ARTHUR MICHAEL AND WIGHTMAN W. GARNER.

The use of potassium permanganate, in aqueous solution, carries with it the formation of a strong alkali, which may act in an undesired manner on the substance to be oxidized; or on the products formed in the oxidation. To obviate this difficulty it has been suggested to carry out the process in the presence of a current of carbon dioxide; or, to add magnesium chloride to the oxidizing mixture and in this way render the caustic alkali inert, inasmuch as it should at once react with the chloride and form the comparatively inactive magnesium hydroxide.¹ A simpler way would be to employ magnesium permanganate as the oxidizer; moreover, the decided tendency of magnesium salts to pass over into magnesium hydroxide when heated with water, seemed to indicate that this salt should possess an unusual capacity for oxidation.

Magnesium permanganate was first prepared by Mitscherlich² and later examined in his laboratory by Aschoff.³ They obtained the salt by treating an aqueous solution of barium permanganate with magnesium sulphate, or the corresponding silver salt with magnesium chloride, and describe it as a deliquescent, crystalline substance, with 6 molecules of water of crystallization. Recently it has been prepared by Chambliss,⁴ by treatment of permanganic acid with magnesium hydroxide; he found that when heated on a water-bath, in aqueous solution, it is rapidly decomposed, giving off oxygen and ozone, and he also called attention to the strong oxidizing power of such a solution.

We first prepared the salt by treating silver permanganate,

¹ Lössen: *Ann. Chem. (Liebig)*, **201**, 370.² Gmelin-Kraut: *Anorg. Chem.*, II², p. 527.³ *Ibid.*⁴ Dissertation, Johns Hopkins University (1900).

suspended in hot water, with an equivalent quantity of magnesium chloride. The first method of Mitscherlich, however, gave better results. Barium permanganate¹ was prepared from the potassium salt, according to the method of Muthmann,² the aqueous solution of the barium salt thus obtained was standardized by means of oxalic acid, and the barium precipitated by the addition of the necessary quantity of magnesium sulphate. The filtrate from the barium sulphate was evaporated on the water-bath to dryness. The product thus obtained has a crystalline structure and bluish-gray metallic luster. In order to completely desiccate the salt it was heated at 100°, in a vacuum, for several days and it appeared to undergo but little decomposition by this treatment. Its metallic luster was not wholly lost, though its color changed from blue to a purplish tint, resembling that of the potassium salt.³

We found anhydrous magnesium permanganate to be insoluble in chloroform, carbon tetrachloride, benzene, toluene, nitrobenzene, ligroin, ether and carbon bisulphide and without action on these compounds at ordinary temperatures, unless some solvent was added to bring about solution of the salt. Methyl alcohol dissolves it in considerable quantity, forming a solution which is tolerably stable at ordinary temperatures, while ethyl and propyl alcohols are attacked instantly. The methyl and ethyl esters of acetic acid dissolve the salt to some extent and form comparatively stable solutions. It also dissolves quite readily in glacial acetic acid and the solution remains unchanged after several hours at room temperature. Propionic acid is attacked more readily, while butyric and isovaleric acids are decomposed with violence and with evolution of carbon dioxide. Acetone dissolves the salt, but is at once attacked with considerable evolution of heat. By way of comparison, it may be mentioned that Peau de Saint-Gilles⁴ found that potassium permanganate is fairly soluble in acetone and

¹ This salt is now a commercial product.

² Ber. d. chem. Ges., 26, 1016.

³ A sealed tube containing some of the salt exploded during the summer, although it was kept in diffused light.

⁴ Ann. Chim. Phys., [3], 55, 396. Sachs: Ber. d. chem. Ges., 34, 497. Such a solution has been employed as an oxidizing mixture, *vide* Sachs: Ber. d. chem. Ges., 34, 497. Michael and Leighton: J. prakt. Chem., 68, 523.

the solution is quite stable even when boiled. Other aliphatic ketones, which are oxidized with difficulty by potassium permanganate, are at once attacked by the magnesium salt; lactic and other hydroxy acids, as well as keto acids, are also immediately destroyed. Of all the solvents examined, only two were found to be sufficiently stable toward the salt to be of any practical use for oxidation purposes, *viz.*, glacial acetic acid and pyridine.

Dissolved in glacial acetic acid, magnesium permanganate is an extremely powerful oxidizing agent. When such a solution is added to benzene, surrounded with a mixture of salt and ice, a constant current of carbon dioxide is evolved. This is a striking fact when the extraordinary stability of benzene toward other oxidizing agents is taken into consideration. Carius¹ oxidized benzene with a mixture of manganese dioxide and sulphuric acid and succeeded in isolating, besides carbon dioxide, formic, benzoic and phthalic acids as products of the oxidation, but these organic acids are all instantly destroyed in the cold by magnesium permanganate in acetic acid solution, and we were unable to separate an intermediate product in the oxidation of benzene to carbon dioxide.

The homologues of benzene show the same conduct towards the solution of the salt as does benzene itself. Moreover, open-chain hydrocarbons, such as hexane, which are also extremely stable towards the usual oxidizing agents, are likewise readily decomposed, yielding carbon dioxide.

Potassium permanganate is almost insoluble in glacial acetic acid, but is fairly soluble in acetic anhydride,² forming a solution which is only slowly oxidized on standing. Such a solution is, however, not to be compared with that of the magnesium salt in glacial acetic acid as regards its oxidizing power. Benzene, toluene and hexane are scarcely attacked in the cold, and even ketones are only oxidized with difficulty.

Magnesium permanganate dissolves more easily in pyridine

¹ Ann. d. Chem., 148, 50. Carius used a mixture of 5 parts sulphuric acid to 1 of water, which dissolved some of the benzene. Although he states that no chemical action takes place when the hydrocarbon dissolves, he does not appear to have examined whether a slow chemical action does not occur.

² It is considerably more soluble in the anhydride than in acetone.

than in glacial acetic acid, but the solution in the former solvent has surprisingly weak oxidizing powers. In fact, those compounds, such as alcohol, acetone and ethyl acetate, which are in themselves solvents for the salt, are acted on less readily in the presence of pyridine than when used alone, that is, pyridine seems to exert an inhibitory influence on the salt as an oxidizer. A solution of the permanganate in a mixture of acetic acid and pyridine is not stable, although either solvent, taken alone, forms a stable solution. Potassium permanganate is also readily soluble in pyridine but, as in the case of the magnesium salt, the solution shows very weak oxidizing powers. Methyl alcohol is more slowly attacked than when treated with the salt alone; acetone is stable as is also ethyl acetate, while ethyl alcohol is oxidized fairly readily. Quinoline dissolves the magnesium salt, but the solution is unstable and this base is also slowly attacked in the presence of pyridine.

From the above-mentioned experiments it appears that anhydrous magnesium permanganate, in some solvents, completely destroys the benzene ring, while pyridine is attacked with very great difficulty. In the aliphatic series the higher hydrocarbons and their derivatives are oxidized very readily to carbon dioxide, whereas the lower members, particularly in the first two carbon series, are comparatively stable. The importance of the nature of the solvent used is strikingly shown in the cases of glacial acetic acid and pyridine. Not only is the pyridine solution surprisingly stable, but the inhibitory effect of the base in preventing otherwise easy oxidations is difficult to understand, especially as there is no evidence of a chemical union between it and the salt.

These preliminary experiments are suggestive along several lines. It would be interesting to ascertain whether magnesium permanganate, in aqueous solution, would show itself so destructive to aromatic substances as it does in acetic acid. That the aqueous solution will prove of use in case of difficultly oxidizable substances and in oxidations where it is desirable to prevent the formation of an alkaline solution, seems

very probable.¹ Again, if substitution products of pyridine are also stable towards the acetic acid solution, the mixture will undoubtedly be of service in the degradation of the many complicated derivatives of the base. The solution of potassium permanganate, in acetic anhydride, may also prove valuable in certain oxidations, as acetic anhydride is not only a ready solvent for many substances that are difficultly soluble in water, but it acts readily on substances containing a hydroxyl or formyl group, to form products that may be less susceptible to oxidation, and the anhydride may, in this way, to a certain extent, protect the intermediary products of oxidation and enable their isolation.

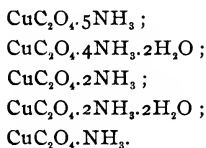
TUFTS COLLEGE, MASS.

ON SOME CUPRAMMONIUM SALTS.

BY D. W. HORN.

The object of this paper² is to call attention to some cuprammonium oxalates that I have obtained and to their bearing on the question of *types* in this class of salts.

The compositions of the oxalates correspond to the empirical formulæ :



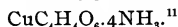
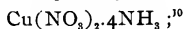
Only the fourth of these has been described previously.

The preparation of the oxalates is a part of a study of those cuprammonium salts that can be obtained from aqueous solutions, with a view to determining whether there is any effect of the acid residue upon the composition or stability of the salt, or of its complex ion.

¹ According to Ullmann and Uzbachian (Ber. d. chem. Ges., 36, 1797) the calcium salt does not seem to be a more powerful reagent than potassium permanganate.

² This paper was read, in part, before the Philadelphia Section of the American Chemical Society, Sept. 21, 1905.

The question of this effect is raised by the differences in physical properties of some cuprammonium salts. It has been shown that the effect of the addition of 4 molecules of ammonia to 1 molecule of copper sulphate, dissolved in water, is to increase the molecular lowering by $7^{\circ}.7$ and the equivalent conductivity by 16.6 reciprocal ohms, whereas a similar addition to copper nitrate, at comparable dilutions, increases the molecular lowering $2^{\circ}.5$ and the equivalent conductivity by 6.9 reciprocal ohms.¹ In the case of copper nitrate, additions of ammonia in excess of 4 molecules to every molecule of dissolved nitrate give normal values for the ratio between the changes in viscosity and in concentration, whereas, under similar circumstances, with copper sulphate the values for this ratio are higher than the normal values.² Cupritetrammonium nitrate can be recrystallized from water;³ cupritetrammonium sulphate is decomposed rapidly by water.⁴ Cupritetrammonium chloride cannot be distinguished from the corresponding sulphate, when the salts are studied as to their effect on the ratio of distribution of ammonia between their aqueous solutions and chloroform.⁵ Cupritetrammonium tartrate is stable in the air and stable in its solutions for a very long time;⁶ the corresponding sulphate decomposes rapidly in the air, and its aqueous solutions deposit basic salts within a day or two.⁷ The formulæ of these salts are :



¹ Reychler: Ber. d. chem. Ges., **28**, 555 (1895).

² Blanchard: J. Am. Chem. Soc., **26**, 1315 (1904).

³ Kane: J. prakt. Chem., **15**, 276 (1838). Ann. Chim. Phys., [2], **72**, 225, 265, 337 (1838).

⁴ Horn and Taylor: THIS JOURNAL, **32**, 253 (1904). Sabbatani: Jahres. d. Chem. **1891**, pp. 1, 777.

⁵ Dawson and McCrae: J. Chem. Soc., **79**, 1072 (1901).

⁶ Schiff: Ann. Chem. (Liebig), **123**, 46 (1862).

⁷ Horn and Taylor: *Loc. cit.*

⁸ Berzelius: Ann. d. Phys. (Gilbert), **40**, 300 (1813).

⁹ Kane: *Loc. cit.*

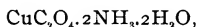
¹⁰ Kane: *Loc. cit.* I have confirmed these formulæ.

¹¹ Schiff: *Loc. cit.*

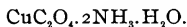
These suggest, as a possible explanation of the difference in behavior, *either* the effect of the "water of crystallization," or the effect of the different acid residues. The matter may be approached experimentally by preparing cuprammonium salts of the several acids under corresponding conditions and comparing them.

I. Dihydrated Cupridiammonium Oxalate.

This is one of the longest known among cuprammonium salts. Vogel¹ obtained it accidentally while trying to make a double oxalate of copper and ammonium. Seubert and Rauter² corrected Vogel's analytical errors and established for the salt the formula



in the place of the one Vogel had assigned, *viz.* :



Preparation.—This salt results when the solution, obtained by treating strong ammonia water with just as much copper oxalate as it can dissolve in the cold, is exposed in an evaporating dish to the air for several hours (Vogel); when a solution of copper oxalate in an excess of ammonia is allowed to evaporate in the air; or when a solution of copper oxalate in concentrated ammonia is diluted cautiously with water (Seubert and Rauter); when a solution of cupritetrammonium sulphate is treated with an equivalent solution of potassium oxalate, in the presence of an excess of ammonia (Kohlschutter).³ Unless precautions are taken, the solution may be heated through 30° or more by the heat evolved as the oxalate dissolves in the ammonia water; so long as the resulting solution is unsaturated with respect to copper oxalate, the same salt separates out when the solution is cooled suddenly as when it cools gradually.

The specimen used in the first two of the following analyses was prepared by the gradual cooling of an unsaturated solution

¹ J. f. Chem. Phys. (Schweigger), 7, 1 (1813).

² Ber. d. chem. Ges., 25, 2821 (1892).

³ *Ibid.*, 37, 1153 (1904).

of copper oxalate in dilute ammonia water, and for the last two analyses the specimen was prepared by rapid cooling of a similar solution.

Weight of salt taken for analysis. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$.
0.3311	14.04	15.42	15.40
0.3478	14.92	15.26	
0.1862	7.94	15.51	
0.2796	13.32	15.20	

Characteristics.—Large, brilliant crystals of this salt form very readily. Vogel described these as short pieces of six-sided, much flattened columns, with two broad sides opposite each other and with four small faces. Seubert and Rauter describe them as "triclinic." A large number of these have been examined with the polarizing microscope and it has been found that they invariably show parallel extinction and the biaxial brush in convergent light; the crystals, therefore, are orthorhombic. The axis of greatest elasticity is parallel to the longest direction of the crystal; that is, presumably, $\mathcal{C} = \overset{1}{\text{C}}$.¹ The crystals effloresce in the air, due to the loss of both ammonia and water. In a desiccator over lime and potassium hydroxide they effloresce so slowly that they may be dried in this way for analysis. If the salt is heated it decomposes gradually at first, but the decomposition soon becomes violent and the specimen that is being heated is scattered. Such a result cannot be avoided even by very cautious heating in hydrogen. The salt has a blue color, quite like that of the crystallized copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Its color could not possibly be confused with the deep purple-blue of the tetrammonium salts like cupritetrammonium sulphate.

II. Anhydrous Cupridiammonium Oxalate.

Preparation.—This compound is formed while a hot, saturated solution of copper oxalate in ammonia water, sp. gr. 0.9, is cooling. A convenient way to obtain it is to filter the hot solution, for the salt separates from the solution with great

¹ I am indebted to Dr. F. Bascom for the examination of the crystals described in this paper.

rapidity and most of it will be found upon the filter. Analysis of an air-dried specimen :

Weight of salt taken. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$.
0.1748	9.10	18.94	18.38
0.2877	14.64	18.51	
Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$.
0.1833	0.0775	33.77	34.24
0.2192	0.0924	33.66	

Some of this same salt may separate from a saturated solution of copper oxalate in ammonia, made for the purpose of preparing the dihydrated salt. In such cases the anhydrous salt always separates first. The following are single analyses of specimens of the anhydrous salt obtained from such solutions :

Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$.
0.0509	0.0217	34.04	34.24
0.2410	0.1022	33.87	

Characteristics.—This salt separates as a sandy powder, which consists of very small crystals that are highly doubly-refracting. They are orthorhombic and the axis of least elasticity is parallel to the longest direction of the crystal ; that is, presumably, $\text{U} = \overset{1}{\text{C}}$. The salt is fairly stable in the air and can be dried for analysis between filter papers. The phenomena that accompany its decomposition by heat are the same, in general, as those accompanying the decomposition of the dihydrated salt, except that the decomposition becomes more violent. The salt exhibits an unusually intense blue color that is very striking and by which it could be distinguished from any other blue salt that I know of.

Vogel probably prepared this salt, but on account of faulty analyses ascribed to it an erroneous formula, *i. e.*, $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$.

This formula appears in some of the reference books.¹ In his paper Vogel states that "if one introduces into a vessel of ammonia water more copper oxalate than the ammonia can dissolve, the copper oxalate on the bottom of the vessel changes into a pulverulent, sandy mass, which is very similar to strongly-colored, dark blue smalt, its color having a great deal of brilliancy (Feuer). From the supernatant mother liquor the efflorescent salt $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ crystallizes subsequently, and then the mother liquor is colored feebly green." It is impossible to draw any conclusion from the results of his analysis; for example, the percentage of copper oxide found by him lies almost exactly half way between the percentage required by the formulæ $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$ and $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$. His description of the physical properties of the substance agrees very closely with the properties of the salt $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$, and the additional fact that the supernatant liquid subsequently yielded the dihydrated salt is entire agreement with the assumption that Vogel had the anhydrous diammonium oxalate. Seubert and Rauter make no reference to this anhydrous diammonium salt, nor to Vogel's description of it. I attempted to reproduce the conditions stated by Vogel; to this end, copper oxalate was ground in a porcelain mortar for more than half an hour with ammonia water, sp. gr. 0.9. After it had been dried over potassium hydroxide, the material thus obtained was analyzed for ammonia. The percentages found were 17.01 and 17.99, values that approach the 18.38 required by the formula $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$. This point is of especial interest because I have obtained a salt of composition represented by the formula $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$, the formula that Vogel erroneously assigned to the intensely blue salt, $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$. As will be seen in the next paragraph, the salt that actually has the formula $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$ differs very much in its properties and preparation from the salt to which Vogel had assigned this same formula.

III. *Cuprimonammonium Oxalate.*

Preparation.—After the mother liquor has completely de-

¹ Handb. d. Org. Chem., Beilstein, 2 ed., I., p. 582. Handwörterb. d. Chem., Ladenburg, VIII., p. 405.

posited the two salts already described, $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$, the residual solution is colored feebly green, as stated by Vogel. If this green liquid is allowed to stand exposed to the air for some time, small crystals of the salt $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$ are formed. These are firmly attached to the walls of the crystallizing dish containing the liquor. The amount of oxalate deposited in this form is relatively small. The following are the results of the analysis of this salt :

Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$.
0.2094	0.0981	37.40	37.71
0.1741	0.0817	37.50	
Weight of salt taken. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$.
0.1569	4.43	10.27	10.37
0.1671	4.86	10.34	

Characteristics.—This salt separates in the form of hard, brilliant, very small crystals. When examined with the polarizing microscope they proved to be orthorhombic and of prismatic habit. The axis of greatest elasticity is parallel to the longest direction of the crystal; that is, presumably, $\text{O} = \overset{\text{I}}{\text{C}}$. The color of the crystals is pale green. When heated, the salt decomposes with violence and leaves a deposit resembling amorphous carbon.

IV. Dihydrated Cupritetrammonium Oxalate.

Preparation.—When a solution of copper oxalate in ammonia water is saturated with ammonia gas, this salt separates out as the concentration of the ammonia in the solution increases. If the original solution is made by taking more than 5 volumes of water to 1 of ammonia water, sp. gr. 0.9, the yield of the salt becomes very small and it is usually necessary to chill the solution in ice-water to obtain any considerable amount of it. In strong solutions the salt may begin to crystallize at temperatures as high as 35° . Analysis :

Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$.
0.3649	0.1124	24.60	24.85
0.4402	0.1358	24.63	
0.4337	0.1339	24.65	

Weight of salt taken. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$.
0.5131	37.63	26.69	26.67
0.5786	42.44	26.69	

Characteristics.—This salt separates from warm, concentrated solutions in crystals that are 2–3 mm. in greatest length. If a mother liquor that is yielding the salt is filtered and evaporated at ordinary temperatures, in a desiccator, over lime, crystal masses as much as 4 cm. in length may be obtained. These crystals cannot be examined except through the glass cover of the desiccator, but, apparently, they are monoclinic, showing orthodome and basal pinacoid and ortho- and clinopinacoids developed in the prismatic zone. The salt is extremely unstable when separated from its mother liquor. It cannot be dried, at ordinary temperatures, with any degree of assurance that decomposition will not set in. It can be dried, however, over lime, in a desiccator kept at about 5° , in an ice-chest. When exposed to the air, even the dry salt decomposes with great rapidity. Its instability was clearly shown in one case, where a glass stoppered weighing tube containing some of the salt was shaken rather violently to break up some lumps of crystals prior to weighing for analysis; the stopper was blown repeatedly from the tube by the ammonia evolved in the rapid decomposition that followed this disturbance. When the decomposition has once been started by any cause, it appears to advance under the conditions in which the salt had previously seemed to be stable. Unlike any of the oxalates previously mentioned, this salt readily parts with its ammonia when it is cautiously heated in hydrogen; under these circumstances the decomposition does not take place with any violence. If heated in the air, however, the decomposition becomes violent.

The color of the salt is deep purple-blue, closely resembling that of cupritetrammonium sulphate.

Kohlschutter in his work realized conditions under which this or some other tetrammonium oxalate was to be expected. He treated cupritetrammonium oxalate, in solution, with an equivalent solution of potassium oxalate, in the presence of an excess of ammonia. The product, however, was the dihydrated diammonium salt. He thinks this result is "clearly to be ascribed to the tendency of the oxalic acid residue to enter into direct union with the copper atom, a tendency that displays itself in the instantaneous combination of the cupric ion with the oxalic acid ion to form the completely insoluble copper oxalate."¹ If such a tendency can be fairly assumed, it is obvious that it has a limit and vanishes under proper conditions.

V. Cupripentammonium Oxalate.

Preparation.—This salt was obtained when a hot, saturated solution of copper oxalate in ammonia water, sp. gr. 0.9, was saturated with ammonia gas as it cooled. Analysis :

Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 5\text{NH}_3$.
0.3466	0.1155	26.62	26.84
0.3797	0.1269	26.69	
0.4343	0.1455	26.75	
Weight of salt taken. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $\text{CuC}_2\text{O}_4 \cdot 5\text{NH}_3$.
0.3340	32.15	35.02	36.01
0.4466	43.15	35.15	
0.3328	32.62	35.66	

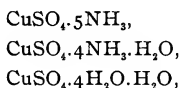
Characteristics.—This salt appears in crystals closely resembling those of the tetrammonium oxalate, but slightly more purple in color. Its instability is very great. Like the tetrammonium salt, it is readily deprived of its ammonia when it is cautiously heated in an atmosphere of hydrogen. When its

¹ Kohlschutter : *Loc. cit.*

solution in warm ammonia water, sp. gr. 0.9, is cooled, the tetrammonium oxalate crystallizes out.

Of these oxalates, the monammonium and pentammonium salts contain copper and ammonia in ratios in which they have never before been observed in salts prepared from *solution*. Two sulphates of corresponding formulæ have been described, but both of these salts have been made only by the action of dry ammonia on anhydrous copper sulphate.

The pentammonium salt *obtained from aqueous solutions* raises the question of the existence of an ion $\text{Cu}(\text{NH}_3)_6^{++}$. As is obvious from the formulæ and from the method of preparation, the case of the oxalates is not analogous to that of the sulphates



from the point of view emphasized by Werner. He represents the one cuprammonium sulphate as $\text{Cu}(\text{NH}_3)_4 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$,¹ which should yield the kathion $\text{Cu}(\text{NH}_3)_4^{++}$; the other cuprammonium sulphate is not assigned a structural formula, but this class of salts is dismissed with the statement that "the number of compounds with the complex (MA_5) is too small to be discussed here at present."² The pentahydrate, however, is represented as $\text{Cu}(\text{H}_2\text{O})_4 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$.¹

The most obvious assumption is that there is an ion $\text{Cu}(\text{NH}_3)_6^{++}$. The existence of this ion has already been assumed by Locke,³ who, in interpreting the values he had found for the "combined ammonia," in ammoniacal solutions of copper sulphate, estimated that about 3 per cent of the total copper must be present in a higher complex, $\text{Cu}(\text{NH}_3)_5^{++}$ or $\text{Cu}(\text{NH}_3)_6^{++}$, when the concentration of copper is 0.1175 molar and that of ammonia normal.

¹ Z. anorg. Chem., 3, 309 (1893).

² Ibid., 2, 303.

³ THIS JOURNAL, 31, 268 (1904).

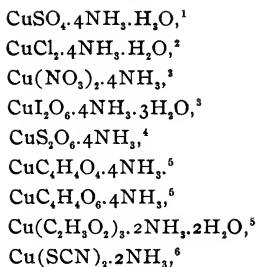
These 5 oxalates do not fit in with the two generally accepted types of cuprammonium compounds that Kohlschutter says are now recognized in most text-books and books of reference. The types are $\text{Cu}(\text{NH}_3)_4\text{X}_2$ and $\text{Cu}(\text{NH}_3)_2\text{X}_2$; they are to be regarded as *fundamental* types because "by far the larger number of cuprammonium salts contain 2 or 4 ammonia groups in the molecule." There is, however, no apparent reason why any one of these 5 oxalates should be assumed to be of a more fundamental type than any other one. It is true that some of them contain copper and ammonia in ratios that are not common, but at present this can as well be regarded as due to the comparatively undeveloped condition of the chemistry of cuprammonium salts as to any assumed peculiarity in copper and ammonia that would cause them to combine more frequently in the ratios 1 : 4 and 1 : 2 than in other ratios.

Any conception of one type as more "fundamental" than any other can be drawn only from comparisons of the formulæ of the cuprammonium salts that are to be found in the records, but it is imperative that only comparable cases should enter as data in such comparisons. Cuprammonium salts that have been separated from solutions containing other salts, or from solutions to which alcohol has been added, cannot, at present, be compared with cuprammonium salts that have separated from solutions containing only the copper salt, ammonia and water. Kohlschutter's work¹ shows that the presence of other salts affects the complexity of the cuprammonium salt that subsequently separates from the same solution, and Dawson and McCrae² have called attention to the probable disturbing influence of alcohol on the equilibrium between copper and ammonia.

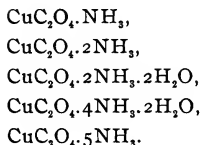
The simple cuprammonium salts that have so far been obtained from aqueous solutions, in the absence of other electrolytes and in the absence of alcohol, are not numerous. They are, so far as I am aware :

¹ *Loc. cit.*

² J. Chem. Soc., 77, 1255 (1900).

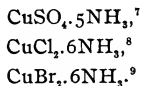


and the oxalates:



The number is scarcely large enough to warrant the assumption of any type as fundamental for *all* cuprammonium compounds.

If we add to these the salts that have been obtained by the action of dry ammonia on anhydrous copper salts, at ordinary temperatures, we find no added reason for assuming any fundamental type. These salts are :



¹ Berzelius : *Loc. cit.*

² Kane : *Loc. cit.*

³ Rammelsberg : *Ann. d. Phys. u. Chem. (Poggendorff)*, **44**, 569 (1838).

⁴ Heeren : *Ibid.*, **7**, 189 (1826).

⁵ Schiff : *Loc. cit.*

⁶ Meitzendorff : *Ann. d. Phys. u. Chem. (Poggendorff)*, **56**, 63 (1843).

⁷ Rose, H. : *Ibid.*, **20**, 150 (1830).

⁸ Bouzat : *Ann. Chim. Phys.*, [7], **29**, 330 (1903). Rose and Bouzat : *Loc. cit.*

⁹ Richards : *Ber. d. chem. Ges.*, **23**, 3790 (1890).

Rammelsberg¹ erroneously assigned to this last salt the formula $\text{CuBr}_2 \cdot 5\text{NH}_3$.

There is no reason to believe that these latter salts are not as truly cuprammonium salts as are those in the preceding list. They simply happen to have been prepared in the absence of water, while the others have been prepared in its presence. Any generalization as to cuprammonium salts must include these compounds, or they must be shown to be a unique class of substances.

I regard it as more profitable, at present, to consider cuprammonium salts from the point of view of the equilibria that exist at the time the salts are forming. This conception has the advantage that it is sufficiently general to include, logically, the salts prepared from aqueous solutions and those prepared from anhydrous salts and dry ammonia, and in that it suggests experimental work that would, necessarily, extend the chemistry of cuprammonium salts. The facts that cupritetrammonium sulphate, chloride, nitrate and oxalate, when brought into the presence of water, at once undergo partial decomposition with the setting free of ammonia, and that, when solutions of copper sulphate, chloride, nitrate and oxalate are saturated with ammonia gas, the corresponding tetrammonium, or higher, salts are forced to crystallize gradually out of the solutions as the concentration of ammonia rises, suggest that cuprammonium complexes are formed only under definite conditions of relative concentrations of water, ammonia and copper salt. The three concentrations referred to are different for different complex salts of the same acid, and are different for the same complex salt of different acids. Thus, if we consider the dihydrated diammonium and tetrammonium oxalates, which are different complex salts of the same acid, obviously, from what has been said of their preparation, there is a higher relative concentration of ammonia and a lower relative concentration of water in the equilibrium equation for the tetrammonium salt than for the diammonium salt. If we consider two pentammonium salts, the same complex salt of different acids, it would seem that the

¹ Ann. d. Phys. u. Chem. (Poggendorff), 55, 247 (1843).

relative concentration of water in the equilibrium equation for cupritetrammonium sulphate is much lower than the relative concentration of water in the equilibrium equation for the pentammonium oxalate, for the oxalate can be obtained from aqueous solutions, while the sulphate requires so low a relative concentration of water that this value has not yet been reached by introducing ammonia gas into an aqueous solution of copper sulphate; so that the pentammonium sulphate has, so far, only been produced under conditions where the relative concentration of water was almost nil, that is, when the anhydrous salt is treated with, approximately, dry ammonia.

It may be that the relative concentration of water is so low in the equilibrium equations for most cupripentammonium and higher cupriammonium salts that it cannot be attained by dissolving ammonia in the aqueous solution of the salt, or that it cannot readily be attained and, therefore, most of the pentammonium salts have not yet been prepared from aqueous solutions. The relative concentration of water is, in general, higher for tetrammonium salts than for pentammonium salts, and in many instances it can readily be attained in solutions, so that there are a number of well known tetrammonium salts that have been obtained from aqueous solutions. There are some instances where one would infer that this value for the relative concentration of water is so low that it is not easily attained by introducing ammonia into an aqueous solution of the copper salt, for in these cases the highest cuprammonium salts, so far obtained from aqueous solution, contain but 2 ammonia groups.

It follows that in systems where the relative concentration of water is very small or almost nil, at least as high cuprammonium salts should be obtained as in systems where the relative concentration of water is as low as it can be gotten by the introduction of ammonia gas into an aqueous solution of the copper salt. That is, the highest salt obtainable by treating the anhydrous salt with approximately dry ammonia must always contain at least as many ammonia groups as the highest salt of the same acid obtainable from aqueous solutions. It is to be expected that the highest salt obtainable by the treat-

ment of anhydrous salt with approximately dry ammonia will, in some cases if not in all, exceed in complexity the highest salt of the same acid obtainable from aqueous solution.

The number of salts that have been prepared from the anhydrous salts by the action of approximately dry ammonia is not large, but in every instance the salt thus obtained does exceed in complexity the highest salt of the same acid obtainable from aqueous solution by the introduction of ammonia gas.

This line of reasoning is consistent as long as there is no experimental fact against the assumption that, between the limits copper salt $+6\text{NH}_3$ and copper salt $+ \text{NH}_3$, only the effects of mass action need be considered, and no such fact is known at present.

This method of consideration presupposes, throughout, that we are dealing with salts prepared at comparable temperatures, in systems containing nothing but copper salt, water and ammonia.

Analytical Methods.

In general, the same methods have been used for determining copper and ammonia as have been described in a previous paper. Slight modifications, however, were adopted.

Because the oxalates could not be heated in the air without violent decomposition, the salts $\text{CuC}_2\text{O}_4 \cdot 5\text{NH}_3$ and $\text{CuC}_2\text{O}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ were heated in hydrogen. The residues, consisting largely of metallic copper, were then heated in the air for half an hour with a view to completely oxidizing, by the copper oxide, any trace of organic matter that might remain after the decomposition in hydrogen. The copper oxide was then converted into cuprous sulphide, by Rose's method, and weighed. In the case of the salts $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$ and $\text{CuC}_2\text{O}_4 \cdot \text{NH}_3$, it was impossible to get rid of the ammonia they contained by heating in the air or in hydrogen, for the decomposition invariably ended disastrously, from the point of view of quantitative analysis. Consequently these salts were treated with a little concentrated sulphuric acid and heated very cautiously until the evolution of gases ceased, the excess of sulphuric acid being subsequently volatilized at a higher tempera-

ture. The residues, consisting of anhydrous copper sulphate, were then converted to cuprous sulphide and weighed. The results for copper run almost uniformly low; I know of no other reason for this than that there may have been small and unavoidable losses of solid matter in both processes by which the salts were freed from ammonia.

The salts were weighed directly into an excess of concentrated hydrochloric acid when they were to be analyzed for ammonia. There was extremely rapid decomposition with loss of ammonia during the weighings of the salt $\text{CuC}_2\text{O}_4 \cdot 5\text{NH}_3$. Concentrated hydrochloric acid was used in the place of sulphuric acid, which had been used in the analysis of the cuprammonium sulphates, because the oxalates can be dissolved in hot, concentrated hydrochloric acid, whereas they are nearly insoluble in sulphuric acid. Better agreement among the results of parallel analyses was obtained when the oxalates had first been dissolved, before the addition of the alkali prior to distillation, than when they had not been dissolved.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
December, 1905.

REPORTS.

Preparation of Pure Ethyl Alcohol.

Commercial "absolute" alcohol always contains water, sometimes as much as 1-2 per cent; in addition to this, aldehyde is frequently present in varying quantity. The methods of purification in general use in laboratories, such as distillation over lime, baryta, sodium, etc., although adequate to remove the water, fail to affect the aldehyde and it cannot be eliminated by fractionation. The problem of its removal has been attacked recently by L. W. Winkler¹ in the following manner: Silver oxide, prepared from the nitrate, is well washed and dried at the ordinary temperature. It is then triturated with a little of the alcohol and the thin paste added to the remainder. The quantity of oxide used depends, of course, on the particular sample of alcohol; it need not exceed a few grams to the liter and may be less. To neutralize the acetic acid which is produced potassium hydroxide, 1-2 grams per liter, is added;

¹ Ber. d. chem. Ges., 38, 3612 (1905).

the mixture is frequently shaken and allowed to remain for several days at the ordinary temperature, until a portion of the alcohol fails to give the test for aldehyde with ammoniacal silver solution.

The author recommends metallic calcium, in the form of filings, for the removal of water from alcohol; 20 grams are usually sufficient to dehydrate 1 liter of commercial "absolute" alcohol. The substances are mixed and boiled in a distillation flask with a reversed condenser and then distilled; cork connections must not be used. The product is 99.9 per cent pure. A second treatment with 0.5 per cent of its weight of calcium appears to remove the last trace of water, because a third treatment, also with 0.5 per cent of calcium, was found to produce no further change. Certain physical properties of alcohol, purified in this manner and fractionally distilled, were determined with the following results: Sp. gr. at $0^{\circ} = 0.80629$, at $10^{\circ} = 0.79787$, at $15^{\circ} = 0.79363$, at $20^{\circ} = 0.78937$; these figures are reduced to a vacuum and referred to water at 4° . The corresponding values given by Mendeléeff are 0.80625, 0.79788, 0.79367 and 0.78945, respectively. The boiling points are $77^{\circ}.81$ (743.5 mm.), $78^{\circ}.20$ (754.9 mm.) and $78^{\circ}.29$ (757.8 mm.); therefore a difference of 1 mm. pressure causes a change of $0^{\circ}.034$ in the boiling point. The author mentions two rather curious facts which he has observed in the course of his work. The reaction between calcium and alcohol is the more vigorous the less water is present below 5 per cent, but ordinary alcohol, containing 5-10 per cent of water, also attacks calcium with considerable energy. Alcohol absolutely free from water is not nearly so hygroscopic as is usually supposed. For example, 200 cc. of it were allowed to remain in an uncovered beaker, exposed to the air of the laboratory, during 15 minutes; it was then found that the amount of water which had been absorbed was less than 0.1 per cent.

J. BISHOP TINGLE.

Stibine and the Allotropic Varieties of Arsenic and Antimony.

In some recent papers,¹ Stock and his assistants describe the methods of preparation and the general properties of several varieties of arsenic and antimony. As a preliminary to this work they made a very careful study of stibine,² which was obtained by the action of hydrochloric acid on an alloy of antimony and magnesium. Its physical constants and chemical and physiological action were worked out in detail. While 1 volume of water only dissolves 0.2 and an equal volume

¹ Ber. d. chem. Ges., 37, 4572; 38, 3837.

² *Ibid.*, 37, 885.

of alcohol dissolves 15 times its volume of the gas, carbon bisulphide dissolves, at 0° , not less than 250 times its volume of stibine. Its most characteristic chemical property is its great instability which, in some cases, produces a violent explosion without any apparent cause, especially during the evaporation of the liquefied gas. It is fairly stable for some hours, at ordinary temperatures, if it is dry and kept in clean vessels, but when the separation of the antimony once begins the speed of the decomposition rapidly increases. Moisture as well as oxygen and, more slowly, air cause a decomposition of the stibine, which is often complete in 24 hours. From a study of its physiological action it was concluded that some of the statements found in the literature regarding its toxicological effects are entirely erroneous. The pure gas when inhaled by mice produced instantaneous death, while exposure, for an hour, to air containing 0.01 its volume of the stibine, in most cases caused death after shorter or longer periods. Although the exact nature of its action is not known, it is, apparently, not due to any reaction with the blood.

The yellow modification of arsenic was first observed in 1867, but very little could be obtained owing to the ease with which it passes over into the black variety. Stock has devised a method by which it is possible to transform the black variety quantitatively into the yellow. A glass tube, sealed at one end, is filled to a height of 2 cm. with "kryptol", which can be heated by means of 2 insulated wires that pass to the top and bottom of the mass and end in two rings, the source of power being a storage battery. About the end of this tube is placed a small beaker containing some black arsenic. This part of the apparatus is introduced into a larger vessel, the joint being ground to make it air-tight. The whole apparatus is then placed in a double-walled vessel into which liquid air can be introduced to cool the inner vessel. If, now, the latter is exhausted and the kryptol is heated, the black arsenic is converted into a vapor and, by contact with the walls of the vessel, which are cooled by liquid air, is suddenly condensed as yellow arsenic. The kryptol is heated to 450° and the action is carried on in a room which is dark, or in one in which the substance is only exposed to red light, as sunlight or the ordinary artificial light changes the yellow variety into the black. The Welsbach light or an electric light causes this conversion slowly, even at the temperature of liquid air, while direct sunlight causes an instantaneous change if the vessel is not in the cooling agent. When the transformation was produced in the dark, by placing the tube containing the yellow arsenic in

a vessel of warm alcohol, there was no evidence of any light formed during the change, although a sharp cracking sound indicated the violence of the action. The authors proved the identity of this substance with that prepared by Erdmann and von Unruh, who obtained it by condensing arsenic vapors in carbon bisulphide and cooling the solution until the yellow arsenic separated out.

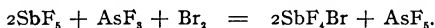
Antimony, like arsenic, exists in a yellow, a black and a metallic-gray variety. The yellow modification can be obtained by passing oxygen or air into liquid stibine at 90° , or by the action of chlorine on stibine at -100° , using liquid ethane as the cooling agent. The substance is only formed in small amounts, and is even more unstable than the yellow arsenic, as it becomes black in a few seconds at -50° . The black variety can be made by three methods: (a) by the transformation of the yellow variety; (b) by the action of oxygen or air on liquid stibine, at temperatures above -90° ; and (c) by the rapid cooling of vapors of ordinary antimony. The variety obtained by these methods is different from the ordinary metallic variety. It has only been obtained in an amorphous condition, is more volatile and has a lower density than the gray, metallic variety. It is also more active chemically, as it is oxidized by air at the ordinary temperature. If the black variety is heated to 400° in a vacuum, it changes, instantaneously, to the gray variety, the appearance and density changing simultaneously, the same result being produced, slowly, by heating with water. The fact that the black variety is unstable even at ordinary temperatures explains why only the gray, metallic variety is found in nature. A substance which has been described by several investigators as black antimony is probably not a pure material.

The three elements, antimony, arsenic and phosphorus exhibit this interesting relation, that while, at ordinary temperatures, in the case of the first the metallic is the stable form, in the second it is the black, amorphous variety, and with the third, in the absence of light, the yellow form, and also the red, which are the more stable.

In this connection mention may be made of a recent article by Ruff and Graf,¹ in which they describe the method of preparation and properties of arsenic pentafluoride. This substance is quite easily obtained and is one of the most active fluorides. When antimony pentafluoride and arsenic trifluoride are brought together at the temperature of liquid air, a crystalline product separates. This is not the pentafluoride, but if bromine is added a heavy white vapor is formed, similar

¹ Ber. d. chem. Ges., 39, 67 (1906).

in appearance to that of sulphur trioxide in the air, and the mass becomes solid. The white vapor is due to the action of moisture on some of the vapors of the arsenic pentafluoride. The reaction can be expressed by the following equation :



If a glass apparatus is used all the connections must be sealed, as contact with organic materials, such as rubber, cork or grease, on stop-cocks will cause the formation of hydrofluoric acid. The apparatus must be most carefully dried to remove all traces of moisture. In order to separate the excess of bromine, the flask is removed from the vessel of liquid air and is allowed to stand until it reaches the temperature of the room, by which time all of the fluoride will have passed over into the receiver, which is cooled by liquid air, the bromine present in excess remaining in the first flask. The fluoride is a colorless gas, which liquefies at -53° and solidifies at -80° . It is easily soluble in water and, when cold, does not attack dry glass. If, however, the glass is moist or the substance is heated, the glass is attacked with the formation of silicon fluoride and arsenic pentoxide. Silicon, when heated with the gas, forms silicon fluoride and arsenic. Sulphur, phosphorus, copper, zinc, iron and bismuth are all acted upon by the gas if heated slightly, while organic substances react very readily.

J. E. G.

REVIEWS.

RADIUM AND RADIO-ACTIVE SUBSTANCES. By CHARLES BASKERVILLE, PH.D., Professor of Chemistry and Director of the Laboratory, College of the City of New York, formerly of the University of North Carolina. Philadelphia: Williams, Brown & Earle. 1905. pp. 154. Price, \$1.00.

In this volume the author has endeavored to present "a non-mathematical work on the subject of radium and its application in medicine," in a popular manner. For all details he refers the reader to the works of Rutherford, Soddy and others. The large number of observations recorded shows that the author has read the subject extensively and the references to the journals containing these would be of great service to the scientific investigator, but, unfortunately, they are honey-combed with errors. The English throughout is bad, even one well acquainted with the subject would have difficulty in interpreting the meaning of many sentences.

The book is divided into two parts, the first, consisting of 5

chapters, on the phenomenon and theories of radio-activity, and the second on the applications of radio-active substances in medicine. This latter portion is, as the author remarks, a collection of observations "impartially reported." In the first section many glaring mistakes occur, of which the following are a few: On p. 14, referring to the properties of β -rays, he says, "they do not discharge the electroscope, hence do not ionize gases," and p. 36, "the term, ray, is applied to a stream of corpuscles." It is considered by the leading physicists that the X-rays and, possibly, the so-called γ -rays are pulses in the ether. Then again, on p. 41, "the penetration of the α -emanations as found is;" and on p. 72 "the phenomenon" of the spinthariscopes "is based upon the bombardment of the zinc sulphide screen by the emanations." Throughout the whole book the words ray and emanation are used more or less synonymously. It is surely unnecessary to say that the emanation from radio-active substances is well defined and is quite distinct from the rays.

Several references are made to the "elements" carolinium and berzelium; it is a pity that time did not permit the author to refer, even in a foot-note, to the work of Meyer and Gumpertz,¹ published February, 1905, which, to say the least, renders the existence of these substances open to the gravest doubt.

The book, as a whole, is uninteresting, without the smallest spark of originality and cannot be of much use. The proof-reading was carelessly done, as mistakes in orthography and proper arrangement of the references abound. The printer, however, has done his work well, the type and paper are good and the illustrations satisfactory.

JAMES BARNES.

SOILS AND FERTILIZERS. By HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Experiment Station. Second edition. Easton, Pa.: The Chemical Publishing Co. 1905. Price, \$1.50.

The first edition of this book appeared in 1899 under the title "The Chemistry of Soils and Fertilizers." In this edition the author has made so many additions and revisions as to materially change the scope of the work and necessitate the change of name. He states that the book, as now presented, includes all of the topics and laboratory practice relating to soils as outlined by the Committee on Methods of Teaching Agriculture, appointed by the Association of Agricultural Colleges and Experiment Stations.

In very clear and simple language Professor Snyder treats

¹ Ber. d. chem. Ges., 38, 817 (1905).

of the physical, geological and chemical properties of the soil, of nitrification, nitrogen of soil, air and farm manures, fixation, the different plant foods and fertilizers, domestic and commercial, the food requirements of crops and rotation and the preparation of soil for crops. The closing chapter contains directions for laboratory practice.

The book assumes that the student has some knowledge of elementary chemistry. It is an excellent manual. E. R.

RESEARCHES ON THE AFFINITIES OF THE ELEMENTS AND ON THE CAUSES OF THE CHEMICAL SIMILARITY OR DISSIMILARITY OF ELEMENTS AND COMPOUNDS. By GEOFFRY MARTIN, B.Sc. (LOND.). London: J. and A. Churchill. 1905. Price, \$4.00.

This book is a study of the chemical affinities of the elements in their periodic relations.

The author's fundamental proposition is that the attractive, or chemical forces of an element determine its chemical properties, *i. e.*, its chemical reactions, its volatility, fusibility, solubility, cohesion, etc., almost exclusively, because the attractive forces of the elements are vastly greater than any other force they exert.

He has compiled tables of data to establish the relative affinities of each element for every other element. This task was only possible, he says, because of the investigations which have been carried on within the last few years on the nitrides, carbides, borides, silicides, etc., of the elements.

Given the data for the relative affinities, it would be possible to express them graphically by series of curves or by surfaces. The author chooses the latter method. He expresses the affinities of elements by lines vertical to a surface. The affinity of chlorine for aluminium, for example, is less than that for sodium, greater than that for sulphur, and the vertical lines expressing these affinities would have lengths relatively proportional to the strength of the affinities.

He takes the Mendeléeff table as a surface. Supposing it is desired to express the affinities of chlorine: Erect on the table vertical lines for each element, placed in the position of the elements on the table. The length of each vertical is proportional to the affinity for chlorine of the element which it represents. Connect the verticals in each "series" of elements by a line passing through their summits, and the verticals ~~are~~, the "groups," by similar lines. The graphical result for the affinities of chlorine for

see end of p 570

H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi		

is a surface as shown in the diagram for chlorine.

The author now arranges these surface diagrams in the order of their elements in Mendeléeff's table. He says they

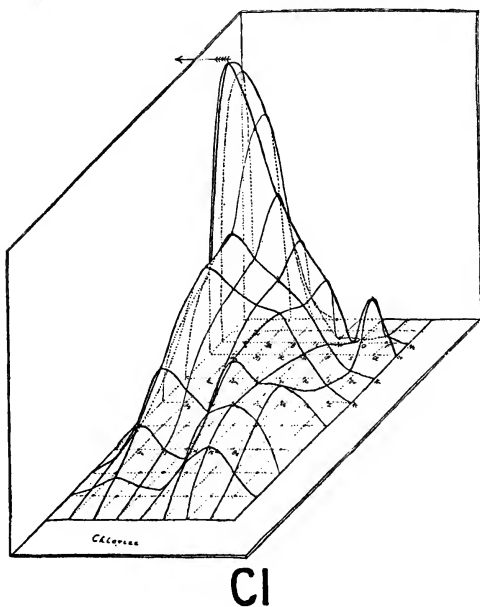


Fig. I.

now "present the appearance of successive positions of an advancing wave whose crest, coming into the field of view on the extreme right hand of the diagram (of a given "series"), gradually sweeps from right to left, altering its form continually as it passes down the field, then passing out of view on

the left. This is followed by the appearance of a new crest on the extreme right (new "series") of nearly, but not quite the original form, . . . each new crest heralding the appearance of a new cycle of elements. At the moment where the one crest passes out of view on the left and a second has not yet made its appearance on the right, we get an element of zero affinity, corresponding to the argon family.

It is difficult to make this quite clear without diagrams of a

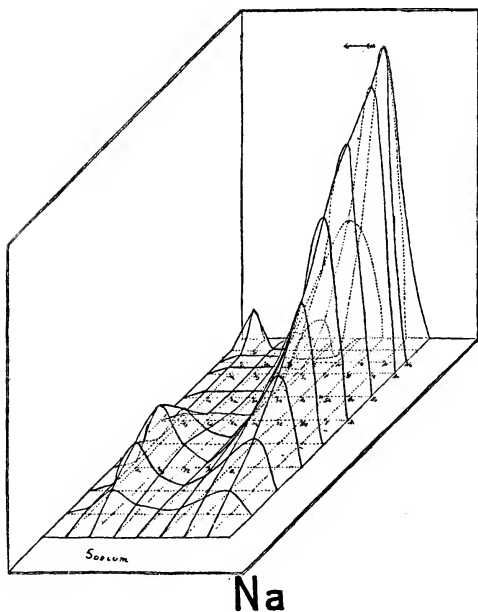


Fig. II.

complete series, which the space for a review will not permit. Diagrams are given of two elements, chlorine and sodium, which elements are at the two extremes of a wave, whose crest is on the left of the chlorine field ; the wave assumes succes-

sive positions as it advances through the elements sulphur \Rightarrow phosphorus \Rightarrow silicon \Rightarrow aluminium \Rightarrow magnesium \Rightarrow sodium, reaching in sodium a crest on the right of the field.

The periodicity of the affinities of elements thus shown, the author calls the "wave law," and he claims that it "explains" the periodic system. He believes that he is the first to discover and point out these relations.

The common wording of the periodic law is "The properties of an element are periodic functions of its atomic weight." Lothar Meyer and Mendeléeff included "attraction" or "affinity" among the properties of the elements, as every chemist knows, therefore, it seems to the reviewer, that the author's claim is unfounded.

The author seems to almost wilfully misunderstand things clear to others, from many examples one will suffice, he says: "It is a wide-spread notion that the molecular weight exercises a predominating effect in determining the melting and boiling points of compounds." Who ever claimed this, save in the case of homologous series of carbon compounds?

In brief, the author so ignores the work of others, puts forward such unwarranted pretensions to originality and, in parts of the book which need not be criticized here, indulges in such wild speculations that one would throw his book aside, were it not for the redeeming fact that he has done a very meritorious and extremely laborious piece of work in compiling the data and building up the diagrammatic surfaces. That the data are as complete as can be obtained at present, that the main conclusions he draws from his data are correct and that his graphic surfaces are an excellent expression of the periodic law, are facts sufficient to render his book noteworthy and valuable.

E. R.

NEUERE ANSCHAUUNGEN AUF DEM GEBIETE DER ANORGANISCHEN CHEMIE. VON PROF. DR. A. WERNER, in Zürich. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1905. pp. xii + 189. Price, unbound, M. 5; bound in linen, M. 5.80.

While the ordinary valence formulas answer very well for most carbon compounds, and even for most inorganic compounds, there are many compounds known, the constitution of which cannot be satisfactorily expressed by means of these formulas. This is not to say that the conception of valence is useless and has been superseded by a better conception. The phenomena of valence are just as real as they ever were, and it is just as important to study these phenomena to-day as it ever was. While we should very much like to know their cause, we may study them without touching the question as to their

cause. We have passed the stage in which it was held that the elements could be rigorously classified under a few heads as univalent, bivalent, trivalent, etc., and that, knowing the valence of the elements, the constitution of the compounds could be deduced. But still we come face to face with valence in every compound and cannot ignore it.

Many efforts have been made to enlarge and improve the conception of valence so as to fit it to certain complex compounds that in its ordinary form it is not competent to explain. Among these efforts that of Professor Werner has, perhaps, attracted most attention. He has shown that the metal-ammonia bases and the double salts can be explained by an interesting extension of the valence hypothesis. His views have been presented in a number of articles which have appeared during the past fifteen years and are well known to chemists. Further, many experimental investigations have been carried out with the object of testing certain conclusions to which Werner's hypothesis leads. This is not the place to discuss the hypothesis. It is sufficient to say that it is of value because it suggests questions that can be answered by experimental means and hence it has contributed and is contributing to the advance of chemistry.

In this book the author has presented his views systematically and clearly and has shown their applicability to the subject of constitution in general. In his preface he says: "It appears to be opportune to present in connected form the views which are to-day of importance for the structural and spatial conception of the molecules of inorganic compounds. We are, however, thoroughly aware that our new conceptions are pictures which, like every other scientific hypothesis, can only serve, as Mach expresses it, to economize thinking and describing. Should these pictures later be replaced by better ones nearer the truth, they will at least have served to pave the way towards a systematization of the almost innumerable facts of inorganic chemistry."

Every chemist ought to study this book. It will not be sufficient to read it.

I. R.

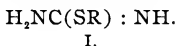
AMERICAN CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

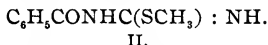
CXXIX.—ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL DIACYLPSEUDOTHIO- UREAS TO ISOMERIC SYMMETRICAL DERIVATIVES.

BY TREAT B. JOHNSON AND GEORGE S. JAMIESON.

In order to show that the free pseudothioureas, I., are quite stable at ordinary temperatures, Wheeler and Merriam¹ treated



pseudomethylthiourea, in aqueous solution, with an *excess* of alkali and benzoyl chloride. They obtained an excellent yield of benzoylpseudomethylthiourea,² II. It has also been shown



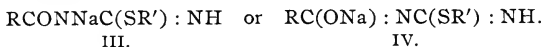
in papers³ from this laboratory that those acylpseudothioureas which contain the grouping—CONH—are soluble in alkali.

¹ THIS JOURNAL, 29, 479 (1903).

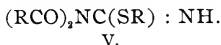
J. Am. Chem. Soc., 23, 293 (1901).

Wheeler and Johnson: THIS JOURNAL, 26, 410 (1901); *Ibid.*, 27, 270 (1902).

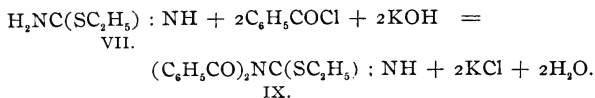
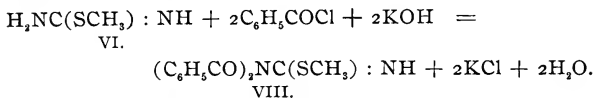
They dissolve with formation of their sodium salts,¹ which can, provisionally, be represented by either of the two formulæ, III. and IV. :



It seemed probable to the writers that a pseudothiurea, I., would react, under proper conditions, with 2 molecular proportions of an acid chloride to give an unsymmetrical diacylpseudothiurea, V. In order to test this assumption we

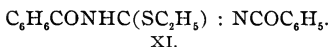
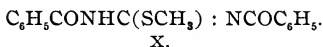


treated pseudomethylthiurea, VI., and pseudoethylthiurea, VII., respectively, in aqueous solution, with the calculated quantity of benzoyl chloride and 2 molecular proportions of potassium hydroxide. They reacted smoothly under these conditions to give the expected unsymmetrical dibenzoylpseudomethylthiurea, VIII., and dibenzoylpseudoethylthiurea, IX., as follows :

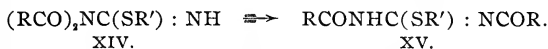
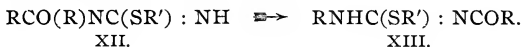


We now find that these two unsymmetrical derivatives, VIII. and IX., are very unstable. When their alcoholic solutions were boiled, or when the compounds were heated to their melting point they were transformed, smoothly, into the stable, symmetrical dibenzoylpseudomethylthiurea, X., and dibenzoylpseudoethylthiurea, XI. :

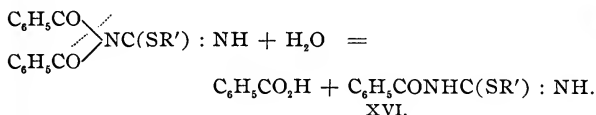
¹ We find that, when benzoylpseudomethylthiurea is warmed in benzene with 0.5 molecular proportion of metallic sodium, it reacts with evolution of hydrogen to give a crystalline sodium salt. We intend to investigate it further. T. B. J.



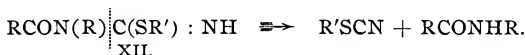
This molecular rearrangement is perfectly analogous to the rearrangement of unsymmetrical acylpseudothioureas, XII., to their isomeric symmetrical derivatives, XIII., which was described by Wheeler and Johnson :¹



These isomeric dibenzoylpseudothioureas, XIV. and XV., are sharply distinguished by their properties, and especially by their behavior with alkali and hydrochloric acid. The labile, unsymmetrical derivatives, XIV., show the behavior of triacid amides and are decomposed by alkali and acids with formation of benzoic acid and the corresponding monobenzoylpseudothiourea, XVI., as follows :



This behavior with alkali is of especial interest when compared with that of the labile acylpseudothioureas,² XII. These were decomposed by alkali with formation of an acid amide and an alkylthiocyanate, according to the following equation :



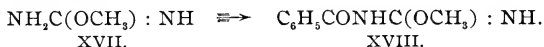
The instability of the labile diacylpseudothioureas, XIV., towards alkali, explains why Wheeler and Merriam³ obtained monobenzoylpseudomethylthiourea when they treated pseudo-

¹ THIS JOURNAL, 27, 270 (1902).

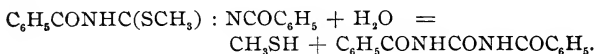
² Wheeler and Johnson : *Loc. cit.*

³ *Loc. cit.*

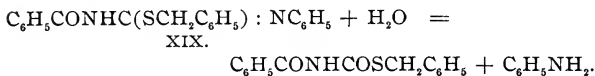
methylthiourea with benzoyl chloride. They state that an excess of alkali was used. Under these conditions, if any of the dibenzoyl derivative was formed, it would be decomposed into benzoic acid and the monobenzoylpseudothiurea. It is of interest to note here that Stieglitz and McKee¹ prepared benzoylpseudomethylurea, XVIII., by treating pseudomethylurea, XVII., with an *excess* of alkali and benzoyl chloride. It seems probable that, under the conditions employed in our experiments, diacyl derivatives will also be obtained in this oxygen series :



The stable symmetrical dibenzoylpseudothiureas, X. and XI., are soluble in alkali and on adding acid unaltered material is precipitated. On the other hand, when boiled with hydrochloric acid they are decomposed with formation of mercaptan and dibenzoylurea as follows :



This behavior with hydrochloric acid is widely different from that of the analogous acylpseudothiureas.² When these are warmed with hydrochloric acid they are decomposed according to the equation :



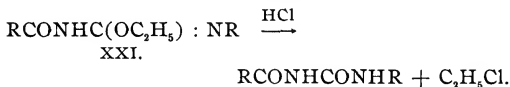
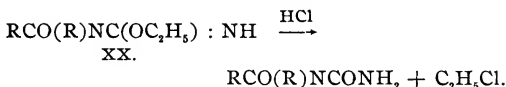
The action of hydrochloric acid on symmetrical diacylpseudothiureas, XV., is perfectly analogous to that of hydrochloric acid on unsymmetrical, XX., and symmetrical, XXI., acylpseudoureas which has been studied by Stieglitz and McKee³ and by Wheeler and Johnson.⁴ They are converted into acylureas with evolution of ethyl chloride as follows :

¹ THIS JOURNAL, 26, 250 (1901).

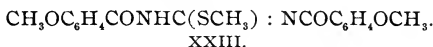
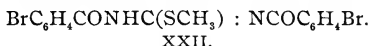
² Wheeler and Johnson: *Loc. cit.*

³ *Loc. cit.*

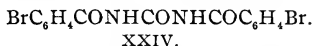
⁴ THIS JOURNAL, 24, 189 (1900) ; 27, 219 (1902).



In the course of our work we investigated the action of parabrombenzoyl chloride and anisyl chloride on pseudomethylthiourea. In these two cases we obtained products which were undoubtedly mixtures of the unsymmetrical and symmetrical diacyl derivatives. When the products were purified by crystallization from alcohol we obtained the stable diparabrombenzoylpseudomethylthiourea, XXII., and dianisylpseudomethylthiourea, XXIII. Their structure was estab-



lished by the fact that they were converted into the corresponding diacylureas, XXIV. and XXV., with evolution of methylmercaptan, when boiled with acids :



EXPERIMENTAL PART.

Unsymmetrical Dibenzoylpseudomethylthiourea,

(C₆H₅CO)₂NC(SCH₃) : NH.—Twenty-five grams of the hydriodic acid salt of pseudomethylthiourea were dissolved in cold water and mixed with a concentrated solution of potassium hydroxide, containing 1 molecular proportion of the alkali (6.4 grams). To the solution were added, alternately, in small portions, 16.1 grams of benzoyl chloride and 6.4 grams of potassium hydroxide, which was previously dissolved in

water. The solution was kept cold by adding ice and was thoroughly shaken after each addition of the acid chloride and alkali. The diacylpseudothiourea separated as a curdy precipitate. After the odor of benzoyl chloride had disappeared the pseudothiourea was filtered off and the filtrate shaken again with 15 grams of benzoyl chloride and 8 grams of potassium hydroxide. We obtained practically as much more of the pseudothiourea as in the first treatment with benzoyl chloride. The product was washed with water and then triturated with ether, to remove any excess of benzoyl chloride. It melted at about 130° – 135° , with slight evolution of methylmercaptan, solidified again, and then partially melted at 145° – 146° to a semisolid, which gradually decomposed on heating and effervesced violently at 175° – 185° . On account of the decomposition of the unsymmetrical derivative at its melting point, and the rapid change into the symmetrical form, it was impossible to obtain a sharp melting point of this compound. It is comparatively stable at ordinary temperatures, and is not rearranged to the symmetrical form by gentle treatment with 95 per cent alcohol. Some of the material that had been allowed to dry in the air for 20 hours was partially dissolved in hot alcohol, and the solution quickly filtered. The part that was not dissolved showed signs of melting at 135° , solidified again and then partially melted at 146° . Analysis:

	Calculated for		Found.
	$C_{16}H_{14}O_2N_2S.$	$C_9H_{10}ON_2S.$	
N	9.39	14.43	9.54

When the alcoholic solution (above) was quickly cooled, the unsymmetrical pseudothiourea deposited in the form of needles and showed the same behavior on melting as the original material. Analysis:

	Calculated for	Found.
	$C_{16}H_{14}O_2N_2S.$	
N	9.39	9.69

Behavior with Alkali.—The unsymmetrical pseudothiourea was insoluble in alkali. Some of the urea was suspended in a cold, 20 per cent sodium hydroxide solution and allowed to stand at ordinary temperatures over night. When examined

the next morning, the pseudothiourea had dissolved with complete decomposition. The odor of methylthiocyanate was not detected.¹ When the alkaline solution was acidified with hydrochloric acid we obtained a crystalline precipitate, that deposited from hot water in plates and melted at 120°. It was identified as benzoic acid. In order to show that, by the treatment with alkali, one benzoyl radical had been removed with formation of benzoylpseudomethylthiourea, the alkaline solution, after filtering from benzoic acid, was treated as follows: It was made slightly alkaline with sodium hydroxide and shaken with a few grams of benzoyl chloride. A crystalline product was obtained which was identified as the unsymmetrical dibenzoylpseudomethylthiourea.

Behavior with Hydrochloric Acid.—When the unsymmetrical pseudothiourea was boiled with hydrochloric acid it was completely decomposed. It dissolved to a clear solution that deposited, on cooling, a crystalline compound which melted at 120°. It was identified as benzoic acid. When mixed with pure benzoic acid the melting point was not lowered. The hydrochloric acid solution was evaporated to dryness, and an oily residue was obtained which gave a strong test for sulphur. It did not solidify on long standing and was extremely soluble in alcohol. On account of the small amount produced it was not further examined.

Behavior on Heating.—Some of the unsymmetrical pseudothiourea was heated in a sulphuric acid-bath at 150°, for 20 minutes. There was a slight evolution of methylmercaptan. The crude product obtained did not show the same behavior as the original material when heated in a capillary tube. It melted at 146°–148°, without effervescence, to a turbid oil. It crystallized from alcohol in long, slender needles, which melted at 147°–148°, to a clear oil. A nitrogen determination agreed with the calculated for *symmetrical dibenzoylpseudomethylthiourea*, $C_6H_5CONHC(SCH_3) : NCOC_6H_5$.

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.39	9.35

¹ Wheeler : *Loc. cit.*

This molecular rearrangement also took place when an alcohol solution of the unsymmetrical pseudothiourea was boiled for a long time. The symmetrical derivative deposited, on cooling, in needles and melted at 147° – 148° , to a clear oil.

Behavior with Alkali.—The symmetrical dibenzoylpseudomethylthiourea dissolves, without decomposition, in a 20 per cent solution of sodium hydroxide. When the alkaline solution was acidified with dilute hydrochloric acid the symmetrical derivative was obtained, melting sharply at 147° – 148° , to a clear oil. Analysis :

	Calculated for $C_{16}H_{14}O_2N_2S$.	Found.
N	9.39	9.3

Behavior with Hydrochloric Acid.—When the symmetrical dibenzoylpseudomethylthiourea was boiled with hydrochloric acid, methylmercaptan was evolved and it was converted, practically quantitatively, into symmetrical dibenzoylurea.¹ It was purified for analysis by crystallizing from acetic acid. It could be made to melt anywhere from 198° to 210° , according to the rate of heating and the size of the capillary tube used. Analysis :

	Calculated for $C_{16}H_{12}O_2N_2$.	Found.
N	10.44	10.41

Unsymmetrical Dibenzoylpseudoethylthiourea,
 $(C_6H_5CO)_2NC(SC_2H_5) : NH$.—This unsymmetrical derivative was obtained when pseudoethylthiourea was treated with benzoyl chloride, under the same conditions as in the preparation of the corresponding dibenzoylpseudomethylthiourea. We used the following proportions: Fifteen grams of the hydrobromic acid salt of pseudoethylthiourea, 22.6 grams of benzoyl chloride and 15.7 grams of potassium hydroxide. The reaction was perfectly smooth and the unsymmetrical derivative separated as an oil, which finally solidified, on continuous agitation. It was washed with cold alcohol and ether, and allowed to dry in the air. It partially melted at 104° – 105° ,

¹ Schmidt : J. prakt. Chem., [2], 5, 58.

then completely solidified in the capillary tube and melted, at 110° , to a clear oil, without effervescence. Analysis :

	Calculated for $C_{17}H_{16}O_2N_2S$.	Found.
N	8.97	8.97

Behavior with Alkali.—The unsymmetrical pseudothiourea was insoluble in a solution of sodium hydroxide. When the alkaline solution was warmed the pseudothiourea was decomposed, with formation of benzoic acid and monobenzoylpseudoethylthiourea. The benzoic acid was identified by its melting point, 120° . The monobenzoylpseudoethylthiourea separated as an oil which would not solidify.

Behavior with Hydrochloric Acid.—Some of the unsymmetrical pseudothiourea was boiled with 20 per cent hydrochloric acid, for 15 minutes. There was immediate decomposition, with formation of a crystalline product and an oil. The oil did not solidify on cooling and was, undoubtedly, monobenzoylpseudoethylthiourea. The crystalline material was filtered off and treated with a dilute solution of sodium hydroxide. A small proportion did not dissolve at once in the alkali and it was separated by filtration. It melted at 110° and was identified as symmetrical dibenzoylpseudoethylthiourea (see below). Its presence here is probably due to the fact that the unsymmetrical pseudothiourea was partially rearranged by the warm acid solution, before being decomposed by the hydrochloric acid. When the alkaline solution was acidified with hydrochloric acid we obtained an immediate precipitate of benzoic acid, which melted sharply at 120° .

Behavior on Heating.—The unsymmetrical derivative is rearranged at its melting point into *symmetrical dibenzoylpseudoethylthiourea*, $C_6H_5CONHC(SC_2H_5) : NCOC_6H_5$. This symmetrical derivative was also easily obtained when the labile modification was crystallized from 95 per cent alcohol. It deposited in needles which melted, at 110° – 111° , to a clear oil. Analysis :

	Calculated for $C_{17}H_{16}O_2N_2S$.	Found.
N	8.97	9.21

Behavior with Alkali.—The symmetrical dibenzoylpseudoethylthiourea is a weak acid. It gradually dissolved in an excess of cold, 20 per cent sodium hydroxide to a clear solution. When the alkaline solution was carefully neutralized with hydrochloric acid, the symmetrical derivative was recovered unaltered. It melted sharply at 110° , to a clear oil.

Behavior with Hydrochloric Acid.—When the symmetrical dibenzoylpseudoethylthiourea was boiled for a long time with hydrochloric acid, ethylmercaptan was evolved, and it was converted, quantitatively, into symmetrical dibenzoylurea.

Symmetrical Diparabrombenzoylpseudomethylthiourea, $\text{BrC}_6\text{H}_4\text{CONHC}(\text{SCH}_3) : \text{NCOC}_6\text{H}_4\text{Br}$.—To an aqueous solution of 10 grams of the hydriodic acid salt of pseudomethylthiourea was added a saturated solution of potassium hydroxide, containing 7.6 grams of the alkali. The alkaline solution was then mixed with 20.1 grams of parabrombenzoyl chloride, which was previously dissolved in benzene. The first addition of acid chloride produced a bulky, gelatinous precipitate. This gradually assumed a granular appearance as we continued to add the chloride, and the solution was thoroughly agitated. The crystalline product was washed with alcohol and dried at ordinary temperatures, in the atmosphere. It melted, when rapidly heated, at 175° – 177° , with some effervescence. This effervescence suggested the presence of some unsymmetrical diparabrombenzoylpseudomethylthiourea. The material deposited from hot, 95 per cent alcohol in needles, that melted at 178° , with slight effervescence, to a turbid oil. Analysis :

	Calculated for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}_2\text{S}$.	Found.
N	6.14	6.17

Behavior on Heating.—Some of the crude diparabrombenzoylpseudomethylthiourea was heated in a sulphuric acid-bath for 1 hour, at 175° . It melted to a turbid oil and very little ethylmercaptan was evolved. The oil solidified at once, on cooling, to a crystalline mass, which deposited from hot alcohol in needles. They melted at 177° – 178° to a turbid oil, with only slight effervescence. When some of this material was

mixed with the crude diparabrombenzoylpseudomethylthiourea, melting at 175° – 177° , the mixture melted at the same temperature, 175° – 177° . Analysis:

	Calculated for $C_{16}H_{12}O_2N_2Br_2S$.	Found.
N	6.14	6.21

Behavior with Alkali.—Diparabrombenzoylpseudomethylthiourea did not show the same behavior towards sodium hydroxide as the dibenzoylpseudothiureas previously described. We could not conclude from its behavior towards alkali whether we were dealing with an unsymmetrical or a symmetrical derivative. It apparently underwent complete decomposition. The only product isolated in a state of purity was parabrombenzoic acid, melting at 250° – 251° . The crude material, melting at 175° – 177° , showed the same behavior towards alkali as did the pure crystallized material obtained after heating for 1 hour, at 175° .

Behavior towards Hydrochloric Acid.—The pseudothiurea was very stable in presence of acids. It was recovered unaltered after boiling with hydrochloric acid for a long time. When it was boiled with hydrobromic acid it behaved as a symmetrical derivative. The crude product, melting at 175° – 177° , and the material obtained after heating in a sulphuric acid bath at 175° , were both converted, practically quantitatively, into symmetrical diparabrombenzoylurea, with evolution of methylmercaptan. It was difficultly soluble in alcohol and acetic acid and decomposed, with effervescence, at 228° – 233° , according to the rate of heating. Analysis:

	Calculated for $C_{16}H_{10}O_3N_2Br_2$.	Found.
N	6.57	6.47

Parabrombenzoylurea, $BrC_6H_4CONHCONH_2$.—This urea was prepared by heating 3 grams of parabrombenzoyl chloride with 0.8 gram of urea at 150° – 155° , for 2.5 hours. It was difficultly soluble in alcohol and water. It deposited from water in microscopic crystals that melted at 236° – 237° , with effervescence. Analysis:

	Calculated for $C_8H_7O_2N_2Br$.	Found.
N	11.52	11.48

Paramethoxybenzoylpseudomethylthiourea, $CH_3OC_6H_4CONHC(SCH_3) : NH$.—This pseudothiourea was prepared as follows: Ten grams of the hydriodic acid salt of pseudomethylthiourea were dissolved in water, with an excess of potassium hydroxide. To this alkaline solution was then added a benzene solution of 7.8 grams of anisyl chloride. The reaction proceeded slowly, and it was necessary to shake for a long time before the odor of anisyl chloride disappeared. Sufficient benzene was added to dissolve all the pseudourea formed. After the reaction was complete the benzene solution was dried over calcium chloride, and then allowed to evaporate spontaneously. We obtained a beautiful deposit of colorless, slender prisms that melted, at 103° – 105° , to a colorless oil. They were very soluble in alcohol. Analysis:

	Calculated for $C_{10}H_{12}O_2N_2S$.	Found.
N	12.50	12.45

Symmetrical Diparamethoxybenzoylpseudomethylthiourea, $CH_3OC_6H_4CONHC(SCH_3) : NCOC_6H_4OCH_3$.—When pseudomethylthiourea was treated, in aqueous solution, with 2 molecular proportions of anisyl chloride and the calculated quantity of potassium hydroxide, it reacted to form a crystalline product that partially melted and decomposed at 145° – 150° . This material was very impure, and was probably a mixture of the monoanisylpseudothiourea and the unsymmetrical and symmetrical dianisylpseudothioureas. Some of the substance was dissolved in warm alcohol. On cooling, needles deposited which melted sharply, to a clear oil, at 159° – 160° . Analysis:

	Calculated for $C_{18}H_{18}O_4N_2S$.	Found.
N	7.82	7.91

Behavior with Hydrochloric Acid.—When the symmetrical pseudothiourea, melting at 159° – 160° , was boiled with hydrochloric acid, mercaptan was evolved. It was converted, quantitatively, into dianisylurea that melted at 205° – 207° , with de-

composition. The urea was difficultly soluble in alcohol, water and acetic acid. Analysis :

	Calculated for $C_{17}H_{16}O_6N_2$.	Found.
N	8.58	8.37

When the crude material, melting at 145° – 150° , was boiled with hydrochloric acid, we obtained a large amount of dianisyl-urea, melting at 205° – 207° . Accompanying this urea was also a small amount of crystalline material which melted at 170° – 175° . This was not examined.

NEW HAVEN, CONN.,
January 3, 1906.

SOME NEW APPARATUS.

BY S. F. ACREE.

A New Form of Alkali Apparatus.

The only excuse for adding another alkali apparatus to the large number already before the chemical world is the fact that not one of those on the market absorbs carbon dioxide rapidly enough to enable us to make combustions accurately, in the common form of furnace, within the period of 1 hour. At the beginning and end of the combustion the carbon dioxide is greatly diluted with air or oxygen, and when this mixture is passed rapidly through the alkali apparatus, some of the carbon dioxide may escape the solvent action of the alkali solution. In the analysis of many compounds the burning must be done slowly, and in such cases the absorption of the carbon dioxide in the alkali apparatus is nearly complete. But in the analysis of substances which burn very smoothly, the writer has found that the great loss of time is that required, not for burning the substance, but for the complete collection of the carbon dioxide. Morse and Taylor,¹ however, have devised a combustion furnace in which the products of combustion are very little diluted with air and oxygen and, as a consequence, the carbon dioxide is much more nearly completely absorbed by any of the common forms of alkali apparatus in a shorter

¹ THIS JOURNAL, 33, 591.

time. Any improvement in the efficiency of an alkali apparatus is, consequently, of great value.

The writer has, therefore, made use of the stability of the Soxhlet alkali apparatus and the fine absorptive efficiency of glass wool, saturated with potassium hydroxide solution, as exhibited in the Wetzel¹ apparatus and has had one constructed according to Fig. I. The outer vessel contains two inner bulbs,

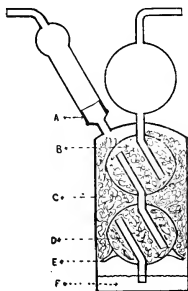


Fig. I.

B and D, connected as in Soxhlet's apparatus. These bulbs are filled with glass wool. Four small glass projections, E, extend from the lower bulb nearly to the wall of the outer vessel; these serve to hold fast the glass wool C, which is wound around the bulbs B and D. The calcium chloride tube, with a ground-glass joint at A, completes the apparatus. When the potassium hydroxide solution is introduced into the vessel, the glass wool inside and outside the bulbs becomes saturated at once with the liquid; the mixture of gases from the combustion tube must filter through all this glass wool and is exposed to such a large surface of alkali solution that the carbon dioxide is practically completely absorbed.

The apparatus can be made in any size desired. The writer uses one $4\frac{1}{2}$ inches high and $1\frac{3}{4}$ inches in diameter. When

¹ Ber. d. chem. Ges., 36, 161.

filled with 50 per cent potassium hydroxide solution, so that the glass wool is saturated and the exit tube from the lower bulb dips into the liquid F, the apparatus weighs 60-65 grams. Not only is the absorption very good, but the apparatus is simple and is not easily broken, a very important point with the student beginning combustion work. The writer has made 8 combustions in one furnace, in a continuous period of 12 hours, by using 2 absorption apparatus.

The efficiency is illustrated by the following tests: During a period of 15 minutes nearly pure carbon dioxide was passed into 2 of these potash bulbs in series; the first one increased in weight nearly 1 gram, but the second did not gain as much as 0.10 milligram. A second experiment was made by passing a stream of gas, consisting of one-third carbon dioxide and two-thirds air, through the series; the first apparatus gained 0.20 gram, but the second one less than 0.10 milligram. A large number of combustions have been made in periods of time varying from 30 minutes to 1 hour, the results, in general, being very satisfactory. The writer feels that the apparatus can be relied upon to absorb the carbon dioxide as rapidly as substances can be safely and completely burned in any combustion furnace.

A Porcelain Lined Bomb for General Laboratory Use.

This bomb has been found to be of such general service in the laboratory that the writer wishes to let others know of its usefulness.

In Fig. II. the bomb E, is made of soft steel, tested to 250 atmospheres water pressure; the wall is approximately $\frac{3}{8}$ inch thick. The white porcelain lining F, has a thickness of $\frac{1}{16}$ inch and can be made of acid-proof or alkali-proof material; it covers the entire inner surface up to the threads at the neck of the bomb. The stopper B, is made of hard bronze, has a square head and screws into the neck of the bomb with heavy threads. The ring C, which is made either of very hard rubber or of lead, makes a gas-tight joint when the stopper is screwed down firmly. The valve consists of the hand-wheel I, attached to the screw A, on a square head. The screw fits

into the stopper with gas-tight threads and packing, shown only roughly in the figure. The screw has a tip D, that can be made of very hard rubber or of lead ; this closes the open-

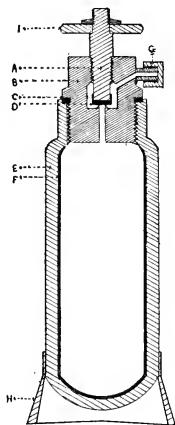


Fig. II.

ing into the bomb so that liquid carbon dioxide cannot escape from the apparatus. If it is desired, this tip D, can be replaced by one of the needle valve style. The inlet (outlet) G, has a cap and is threaded to fit carbon dioxide cylinders ; this threading can, of course, be made to order. The bomb rests in a ring base H, which can be removed readily.

The apparatus can be made in any size. The ones in use in this laboratory are about 10 inches in total height, 3 inches in outside diameter, and hold 430 cc. The mouth is $1\frac{1}{2}$ inches in diameter and allows the easy introduction or removal of the substances to be used in the bomb.

The writer had this form of bomb made for use in experiments in which dry, liquid carbon dioxide was allowed to react with other substances in absolute ether. A piece of Manasse steel tubing, 1 inch outer diameter and 2 feet long,

properly threaded and tested to 100 atmospheres gas pressure, is used to connect the bomb to the carbon dioxide cylinder. This steel tube is filled with a long layer of calcium chloride next to the cylinder and a short layer of phosphorus pentoxide next to the bomb. When the bomb is cooled with salt and ice 100 grams of carbon dioxide can be introduced into it in 10 minutes, and the liquid is so nearly free from water that bright sodium wire is hardly affected by it in a week. When closed tightly, the bomb has stood 2 months, containing 100 grams of liquid carbon dioxide, without losing 1 gram.

The use of ether in the apparatus for 1 year has not appreciably affected the hard rubber ring and tip C and D, but it is certainly preferable to have these made of lead if organic solvents are to be used in the bomb, or if the apparatus is to be subjected to high temperatures.

It is evident that such a bomb is very serviceable for storing small quantities of gases, such as sulphur dioxide, ammonia, etc., that liquefy only under pressure or at low temperatures. The apparatus is convenient for use in the study of reactions in which gases are liberated; they can be drawn off at will and examined.

The bomb has proved to be especially serviceable in place of sealed tubes. The substances which are to react are introduced into the bomb, which is closed by means of a vise and a wrench. The heating is carried out in a water- or oil-bath. Substances which it is desired to mix in the bomb, after the latter has been closed, may be placed, in the usual manner, in thin-walled glass tubes, which are subsequently broken.

Apparatus for Rapid Precipitations in Electrolytic Analysis.

The apparatus is shown in Fig. III. K is a round, platinum gauze electrode, 2.5 inches in diameter. It consists of an outer ring forming one piece with the arm G, and an inner, removable ring which holds the gauze in position. The two rings can be held firmly together by means of fine platinum wire or 4 small drops of gold; it was found that the gold was

hardly affected by the solutions. The gauze is made of number 30 platinum wire, and there are 50 meshes to the linear inch. The arm G, is of number 16 platinum wire and is held

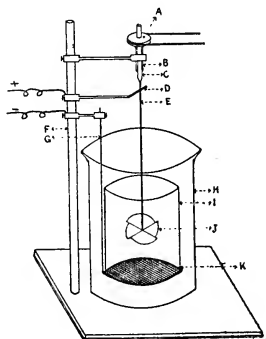


Fig. III.

in position by a binding post attached to the glass rod F. The electrode K, is kept $\frac{1}{2}$ inch from the bottom of the beaker H, and supports the glass cylinder I, which has the same diameter as K, and, therefore, rests on the outer ring of K. The cylinder I, is completely submerged, the upper edge being at least $\frac{1}{4}$ inch under the surface of the liquid. It is better to have several cylinders I, of various heights, to correspond to different volumes of liquid to be electrolyzed. The rotating, propeller-like electrode J, is made of heavy platinum foil and is riveted to the platinum rod E. E is sealed into the glass tube C, which is rotated in the glass tube B, by means of the pulley A, and a Rabe water turbine or a small electric motor. A platinum strip or a number 16 wire D, brushes against E, under the solution, and is connected to a binding post on F; this contact between D and E is excellent. The distance between K and J depends entirely upon the required voltage and the strength of the current to be used, and can be regulated at will. The beaker H, rests on the base of the

stand, or upon an asbestos board on a ring fitted to F if the solution is to be heated by a small burner.

The new and important feature of this apparatus is that the rotating disk J, forces all of the solution downward through the gauze K, up between the walls of H and I, and back down through K again. All of the liquid is thus brought close to the electrode K, as frequently as is wished.

At the end of the analysis the rotation of J is stopped, but the passage of the current continued; the liquid is siphoned out between H and I, while distilled water, or any other desired liquid, is poured into I. In this way the electrolyzed solution is easily removed without danger of the loss of the precipitated metal.

The conditions of voltage, current, temperature, etc., used in this apparatus are essentially those given in any good text-book, such as Classen's "Electrolytic Analysis."

This form of electrolytic apparatus was first made and used by the writer in the University of Utah, in 1901. At that time Perkin's¹ article describing his use of gauze electrodes had not appeared. The one described above is as simple in construction as any illustrated by Perkin, and has the decided advantage that the rotating electrode has excellent electrical contact without recourse to the expensive rotator used by him. The most important feature of this apparatus, however, and one which differentiates it from any yet described, is that all of the solution to be electrolyzed is forced by the rotating electrode into contact with the gauze as often as is wished, and the metal is more rapidly precipitated.

The apparatus has proved to be of great service in the rapid estimation of all the common metals, such as copper, silver, etc., and is especially useful in those analyses in which a metallic oxide—that of lead or of molybdenum²—is precipitated on the gauze. Analyses have often been made in 30 minutes in this apparatus, whereas the duplicate, electrolyzed in a beaker with a platinum cone or in a platinum dish, required 1–2 hours. Copper and lead dioxide are precipitated on

¹ Chem. News, 88, 102.

² Smith and Kollock: J. Am. Chem. Soc., 23, 669.

K in a hard coating, and very rarely in the spongy layer so often formed on a dish when the analysis is made too rapidly. The apparatus has proved to be as satisfactory in the hands of students, as regards accuracy of analysis, as platinum dishes, and a great saving of time is effected. The electrode is easily cleaned, dried and weighed, and the gauze is not readily injured. The cost is very much less than that of a platinum dish of 100 cc. capacity. The use of this electrode is especially advantageous with dilute solutions; the liquid can be electrolyzed directly, without evaporating it to the small volume necessary when dishes are used.

In the analysis of lead solutions it was found better to slip a piece of narrow, thin glass tubing, nearly the length of G, over this arm and fuse it to G close to K; in this way the precipitate was confined to K and the lead dioxide was afterwards dried by heating the electrode at 180° , in a beaker.

Any of the pieces of apparatus described in this paper can be purchased from Messrs Eimer and Amend.

JOHNS HOPKINS UNIVERSITY,
January 1, 1906.

ON THE FORMATION OF ALCOHOLATES BY CERTAIN SALTS IN SOLUTION IN METHYL AND ETHYL ALCOHOLS.

[FIFTEENTH COMMUNICATION.]

BY HARRY C. JONES AND LEROY McMASTER.

It was shown by Jones and Getman¹ that a large number of salts have the power to combine with water when dissolved in that solvent. Indeed, this property is possessed by salts in general, although in very different degrees. Those salts that have the greatest power to combine with water as water of crystallization, have, as a rule, the greatest power to combine with water in aqueous solution.

Having established this fact in aqueous solutions, the question naturally arose, do salts have the power to combine with

¹ THIS JOURNAL, 31, 303 (1904).

any solvent other than water when dissolved in the solvent in question?

To throw light on this point, some work was carried out by Jones and Getman,¹ using ethyl alcohol as the solvent, and lithium chloride and nitrate, and calcium nitrate as the dissolved substances. In still earlier work Jones and Getman² used ethyl alcohol as the solvent, and potassium iodide, sodium iodide, ammonium iodide, cadmium iodide and sodium bromide as the dissolved substances.

The results show, in general, that the molecular rise of the boiling point of the solvent produced by the dissolved substance is greater than the theoretical molecular rise for ethyl alcohol, either as found by direct experiment in dilute solutions of non-electrolytes in the solvent in question, or as calculated by the equation

$$C = \frac{2 T^2}{100 L}.$$

In a number of the above cases very marked differences manifest themselves—differences which are far too large to be accounted for on the basis of the dissociation of the dissolved substance.

Take the case of lithium chloride in ethyl alcohol, as worked out by Jones and Getman.³ The molecular rise of the boiling point is not only greater than the theoretical rise at nearly all of the concentrations employed, taking into account, of course, the dissociation; but the molecular rise increases rapidly with the concentration of the solution. Thus from 0.07 N to 2.07 N the molecular rise of the boiling point produced by lithium chloride increases, with a fair degree of regularity, from 1.28 to 2.43. As the concentration of the solution increases the dissociation, of course, decreases, and this would tend to cause the molecular rise to decrease with increasing concentration.

¹ THIS JOURNAL, 32, 338 (1904).

² *Ibid.*, 31, 338 (1904).

³ *Ibid.*, 32, 339 (1904).

Notwithstanding this influence, we have just seen that the molecular rise increases rapidly with increase in the concentration of the solution. Since, in the preparation of the solutions, both solvent and dissolved substance were taken in weighed quantities, the question of the change in the specific gravity of the solutions does not come into play.

Jones and Getman¹ interpreted their results by the boiling point method, in ethyl alcohol as the solvent, in the same manner that they had previously interpreted their results by the freezing point method in aqueous solutions. The abnormally great rise in the boiling point of ethyl alcohol, produced by certain salts, was due to combination between the dissolved substance and part of the solvent—to the formation of alcoholates in solution. The part of the alcohol which was in combination with the dissolved substance would thus be removed from the field of action as far as solvent is concerned. There being less alcohol present acting as solvent, the rise in the boiling point produced by the dissolved substance would be, of course, greater than if all the alcohol was playing the rôle of solvent.

This suggestion accounts for the facts in the case of solutions in alcohol, just as the hydrate theory had explained the abnormally great lowering of the freezing point of water produced by a large number of salts, especially when the concentrations were great.

The object of the present investigation is to extend the earlier work of Jones and Getman to a larger number of salts, and to more than one non-aqueous solvent. We have repeated the work, in ethyl alcohol, with a few of the same substances that were employed by Jones and Getman, and have added a number of others to the list of those that were earlier studied.

We have worked with lithium chloride, lithium bromide and lithium nitrate in methyl alcohol; and with lithium chloride, lithium bromide, lithium nitrate and calcium nitrate in ethyl alcohol.

In making the boiling point measurements, the boiling point apparatus of Jones² was employed. In order to be independent

¹ THIS JOURNAL, 32, 342 (1904).

² *Ibid.*, 19, 581 (1897).

of correction for changes in the barometer, two pieces of boiling point apparatus were used. In one of these the pure solvent was boiled and in the other the solution.

The alcohols used in this work were dehydrated by the usual methods, and care was taken to keep them free from moisture when transferred to the boiling point apparatus. The conductivity of the methyl alcohol, at 25° , was 2×10^{-6} , and that of the ethyl alcohol from 1 to 2×10^{-6} . The salts were all completely freed from water.

The usual precautions were taken in making the boiling point measurements, and the proper correction applied for the solvent that existed in the apparatus in the form of vapor. The top of the condenser was closed by means of a tube filled with calcium chloride, to prevent the moisture in the air from coming in contact with the alcohol in the boiling point apparatus.

In the following tables m is the concentration in terms of gram-molecular normal. This was obtained by dividing the number of grams of salt in 1000 grams of the solvent by the molecular weight of the salt; ρ is the corrected rise in the boiling-point of the solvent, produced by the dissolved substance at the concentration in question; $\frac{\rho}{m}$ is the molecular rise in the boiling point of the solvent at the given concentration.

The results for lithium chloride, bromide and nitrate are given in Tables I. to III. Calcium nitrate, in methyl alcohol, could not be satisfactorily studied on account of its limited solubility in this liquid.

Results with Methyl Alcohol.

The constant for methyl alcohol is 0.84. By comparing with this value, the molecular rise found, we can see at once the magnitude of the discrepancy between the value obtained experimentally and the theoretical value for an undissociated substance. All three of the following salts are, of course, disso-

ciated to a greater or less extent by methyl alcohol. This, however, would scarcely account for the magnitude of the molecular rise even in the most dilute solutions, since the dissociating power of methyl alcohol is only from one-third to one-half that of water. Dissociation is entirely incapable of accounting for the *increase in the molecular rise with increase in the concentration of the solution* which, we see from the results, takes place in the case of all three of the above salts. The dissociation would decrease with increase in the concentration, which would tend to diminish the magnitude of the molecular rise of the boiling point as the solutions became more and more concentrated.

Attention should also be called to the *magnitude of the molecular rise* in the most concentrated solutions employed. In such solutions it is almost *twice* the boiling point constant, or normal molecular rise for this solvent. The dissociation in such solutions is certainly not greater than between 30 and 40 per cent.

Table I.—*Lithium Chloride in Methyl Alcohol.*

<i>m.</i>	<i>p.</i>	$\frac{p}{m}$.
0.0453	0.061	1.34
0.1050	0.140	1.33
0.1377	0.181	1.31
0.2404	0.313	1.30
0.2598	0.340	1.31
0.2891	0.380	1.31
0.3188	0.424	1.33
0.3965	0.529	1.33
0.4557	0.610	1.34
0.4921	0.660	1.34
0.4964	0.670	1.35
0.5762	0.779	1.35
0.6919	0.973	1.40
0.7522	1.068	1.42
0.7717	1.100	1.42
0.7961	1.139	1.43
0.8635	1.250	1.44
0.9258	1.347	1.45
1.0074	1.512	1.50
1.1847	1.838	1.55

Table II.—*Lithium Bromide in Methyl Alcohol.*

<i>m.</i>	ρ .	$\frac{\rho}{m}$.
0.0919	0.129	1.40
0.1409	0.192	1.36
0.1780	0.241	1.35
0.1970	0.270	1.36
0.2514	0.344	1.37
0.2557	0.351	1.37
0.2727	0.377	1.38
0.3101	0.412	1.33
0.3689	0.499	1.35
0.5554	0.756	1.36
0.6108	0.846	1.38
0.6182	0.858	1.38
0.6654	0.927	1.39
0.5882	0.808	1.37
0.6745	0.965	1.43
0.8571	1.287	1.50
1.2128	1.970	1.62

Table III.—*Lithium Nitrate in Methyl Alcohol.*

<i>m.</i>	ρ .	$\frac{\rho}{m}$.
0.0961	0.120	1.24
0.1369	0.163	1.19
0.1437	0.171	1.19
0.1711	0.202	1.18
0.2089	0.248	1.18
0.2367	0.286	1.21
0.2830	0.354	1.25
0.3744	0.475	1.26
0.4454	0.568	1.27
0.4504	0.575	1.27
0.4709	0.607	1.28
0.5300	0.684	1.29
0.6122	0.792	1.29
0.7338	0.976	1.33
0.7538	1.004	1.33
0.8342	1.132	1.35
0.9212	1.265	1.37
1.1320	1.563	1.38

We interpret these results in terms of the same theory that was advanced by Jones¹ in connection with aqueous solutions. There is combination between the solvent and the dissolved substance, forming, in the case of water, *hydrates*; in the case of alcohol, *alcoholates* in solution. As the concentration of the solution becomes greater, more and more alcohol is held in combination by the dissolved substance, consequently, there is less and less alcohol acting as solvent and the molecular rise in the boiling point, therefore, increases.

Results with Ethyl Alcohol.

The results in ethyl alcohol, obtained with lithium chloride, lithium bromide, lithium nitrate and calcium nitrate are given in Tables IV. to VIII.

We obtained results of the same general character as those found by Jones and Getman for the substances with which they worked in ethyl alcohol. The constant for ethyl alcohol is 1.15. If we examine the results for lithium chloride, bromide and nitrate, we shall find the molecular rise in the boiling point, especially in the more concentrated solutions, to be much greater than this value. Further, the molecular rise increases with the concentration of the solutions. The results

Table IV.—Lithium Chloride in Ethyl Alcohol.

<i>m.</i>	<i>ρ.</i>	$\frac{\rho}{m}.$
0.1356	0.191	1.408
0.3692	0.555	1.503
0.3958	0.595	1.503
0.5084	0.765	1.504
0.5350	0.803	1.500
0.5407	0.812	1.502
0.6478	1.025	1.582
0.6771	1.080	1.595
0.7577	1.218	1.607
0.8083	1.320	1.633
0.8235	1.347	1.635
0.8529	1.401	1.642
0.9035	1.495	1.650

¹ THIS JOURNAL, 23, 103 (1900).

Table V.—*Lithium Bromide in Ethyl Alcohol.*

<i>m.</i>	<i>p.</i>	$\frac{p}{m}$.
0.0762	0.096	1.276
0.1942	0.300	1.544
0.3390	0.514	1.516
0.3544	0.530	1.495
0.4387	0.675	1.538
0.5731	0.914	1.594
0.5892	0.945	1.604
0.6072	0.978	1.610
0.6280	1.000	1.629
0.7640	1.263	1.653
1.0336	1.935	1.872
1.0510	1.923	1.875
1.0530	1.981	1.881
1.1030	2.134	1.940
1.1730	2.325	1.982

Table VI.—*Lithium Bromide in Ethyl Alcohol (Second Series).*

<i>m.</i>	<i>p.</i>	$\frac{p}{m}$.
0.1126	0.140	1.24
0.1890	0.270	1.45
0.3815	0.550	1.44
0.4161	0.617	1.48
0.4476	0.665	1.48
0.5788	0.880	1.52
0.6513	1.031	1.58
0.7031	1.151	1.63
0.8312	1.441	1.73
0.9950	1.798	1.81
1.3142	2.655	2.02

Table VII.—*Lithium Nitrate in Ethyl Alcohol.*

$m.$	$\rho.$	$\frac{\rho}{m}.$
0.0815	0.103	1.280
0.1423	0.187	1.314
0.2990	0.421	1.407
0.3088	0.435	1.408
0.3234	0.459	1.420
0.3370	0.479	1.420
0.5377	0.776	1.440
0.6297	0.920	1.460
0.7330	1.072	1.460
0.7962	1.165	1.460
0.8444	1.241	1.470
1.1770	1.800	1.530
1.2530	1.951	1.557

Table VIII.—*Calcium Nitrate in Ethyl Alcohol.*

$m.$	$\rho.$	$\frac{\rho}{m}.$
0.0428	0.057	1.33
0.0594	0.078	1.31
0.1137	0.135	1.18
0.1153	0.138	1.19
0.1981	0.239	1.20
0.2161	0.253	1.17
0.2590	0.300	1.16
0.2920	0.333	1.14
0.2964	0.340	1.14
0.3081	0.351	1.14
0.3380	0.383	1.13
0.3486	0.395	1.13
0.3815	0.425	1.11
0.3978	0.444	1.11
0.5361	0.582	1.08
0.5680	0.620	1.09
0.6862	0.740	1.08
0.7029	0.750	1.07
0.8274	0.885	1.07
0.9118	0.972	1.06

in the more dilute solutions in ethyl alcohol might be partially explained on the basis of dissociation, since ethyl alcohol has about one-fourth the dissociating power of water. Dissociation, however, is incapable of explaining the magnitude of the molecular rise in the more concentrated solutions, and is entirely incapable of explaining the fact that the molecular rise of the boiling point increases with the concentration of the solution, up to the most concentrated solutions that were employed.

Calcium nitrate is an exception to the above relations, as was found earlier by Jones and Getman.¹ This was rather surprising, so we repeated the work and obtained essentially their results. The molecular rise in the boiling point of ethyl alcohol, produced by calcium nitrate, decreases, with a fair degree of regularity, from the most dilute to the most concentrated solution studied. In the most concentrated solutions the molecular rise becomes less than the theoretical value, 1.15, notwithstanding the fact that in such solutions we have quite appreciable dissociation. The conclusion to which we seem to be forced by the results is that calcium nitrate in ethyl alcohol is somewhat polymerized. We probably have also combination between the solvent and the salt, but this is more than overcome, as far as the effect on boiling point is concerned, by the polymerization of molecules of the salt itself, forming more complex aggregates than would be expressed by the simple formula $\text{Ca}(\text{NO}_3)_2$.

The conclusion to which we are led by the results, in general, in ethyl alcohol, is the same as that to which we have already referred in the case of solutions in methyl alcohol. The large value of the molecular rise in the more concentrated solutions would indicate that a part of the alcohol was not playing the rôle of solvent, but was combined with the dissolved substance. This would also account for the increase in the molecular rise of the boiling point with increase in the concentration of the solution, notwithstanding the fact that the dissociation is decreasing as the solution becomes more concentrated. As the amount of dissolved substance present in-

¹ THIS JOURNAL, 32, 338 (1904).

creases, the total amount of the solvent combined with it increases, and less and less alcohol is acting as solvent as the concentration becomes greater and greater. This is in keeping with the law of mass action. The amount of the solvent combined with 1 molecule of the dissolved substance is probably greater the more dilute the solution, at least up to a certain point. We have not yet been able to work out even the approximate composition of the alcoholates formed, as Jones and Getman¹ and Jones and Bassett² have done in the case of aqueous solutions. This is due, in part, to the fact that we have not yet had time to determine accurately the dissociation of the various salts at the different dilutions in the alcohols. When such data shall have been secured, there ought to be no very serious difficulty in calculating the approximate composition of the alcoholates formed by the various salts in solution in these solvents. Work is now in progress on this and similar problems.

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RELATIVE RATES OF OXIDATION OF ORTHO, META AND PARA COMPOUNDS.

BY HAMILTON BRADSHAW.

In 1887 Dreyfus³ determined the rate at which various organic compounds are oxidized by potassium permanganate. If n grams of a substance are required to reduce a quantity of potassium permanganate equal to that reduced in the same length of time by 1 gram of ethyl alcohol, then $1/n$ expresses, in a manner, the relative rate of oxidation of the substance. Dreyfus made his measurements in acid solution and used a very dilute solution of potassium permanganate, 1 cc = 0.0001 gram of crystallized oxalic acid. He found that the value of $1/n$ for the substances which he studied varies from 0.2 to 10,000. With the dihydroxybenzenes the rates of oxidation are in the ratio—ortho : meta : para : : 5000 : 2000 : 3333. For

¹ THIS JOURNAL, 31, 303 (1904); 32, 308 (1904). Z. physik. Chem., 49, 385 (1904).

² THIS JOURNAL, 33, 334 (1905).

³ Compt. rend., 105, 523.

the toluidines he found the ratio—ortho : meta : para :: 17.8 : 9.09 : 12.5.

The present investigation was undertaken, at the suggestion of President Remsen, to determine the rates of oxidation of certain isomeric organic compounds of the ortho, meta and para series. It was thought that a comparison of the behavior of several groups of such isomeric compounds might possibly reveal some tendency which would admit of general expression.

The compounds which were studied for this purpose are all easily prepared. Those that were obtained from the laboratory stock were purified by crystallization or distillation. The following is a list of the substances used, together with their melting-points (uncorr.) :

	Melting point.
Salicylic acid	155°-156°
<i>m</i> -Hydroxybenzoic acid	198°-199°
<i>p</i> -Hydroxybenzoic acid	210°
Anthranilic acid	145°
<i>m</i> -Aminobenzoic acid	173°
<i>p</i> -Aminobenzoic acid	186°
<i>o</i> -Nitrophenol	45°-46°
<i>m</i> -Nitrophenol	95°-96°
<i>p</i> -Nitrophenol	112°-113°
<i>o</i> -Nitraniline	73°-74°
<i>m</i> -Nitraniline	112°
<i>p</i> -Nitraniline	147°
<i>o</i> -Toluidine	
<i>m</i> -Toluidine	
<i>p</i> -Toluidine	45°

Parahydroxybenzoic acid was made by fusing parasulphaminebenzoic acid with a mixture of sodium and potassium hydroxides.

Of all these substances, except the nitranilines, aqueous solutions were made, containing 1 gram to the liter. Only 0.5 gram of the nitranilines was dissolved in a liter of water, on account of the slight solubility of these compounds, but twice as much of the solution was used in each experiment. The

toluidines were dissolved by adding sufficient sulphuric acid to form the neutral salts. The solution of potassium permanganate used for the oxidations contained 4 grams of potassium permanganate to a liter of water. The procedure was as follows: A fixed amount of the solution of the organic substance was diluted to a definite volume and a quantity, usually 15 cc., of the solution of potassium permanganate was added from a burette. After allowing the mixture to stand for a certain length of time, the excess of potassium permanganate was determined. At first this was done by adding an excess of a solution of manganous sulphate, free from iron, and filtering off the precipitated oxides of manganese on an asbestos plug. By dissolving in a known quantity of a standard solution of oxalic acid, or of ferrous ammonium sulphate, and titrating the excess of reducing substance, the amount of available oxygen in the precipitate was determined, and, by subtraction, the oxygen used in the oxidation of the organic compound.

It was found, however, that this method does not give satisfactory results, probably on account of a loss of oxygen in heating the solution to dissolve the oxides of manganese. The method finally decided upon for the determination of the un-reduced potassium permanganate, is that based on the liberation of iodine from potassium iodide by potassium permanganate, in the presence of an acid. At the end of the oxidation period an excess of a solution of potassium iodide and dilute hydrochloric acid was added to the mixture and the liberated iodine determined by titration with a solution of sodium thiosulphate, previously standardized against the solution of potassium permanganate by the same method.

In the case of the nitranilines the end product was not very definite. Apparently some oxidation product continued to liberate iodine and, consequently, the quantity of thiosulphate used was too great, although the titrations were made as rapidly as possible. The figures expressing the amounts of potassium permanganate reduced are, therefore, uniformly low for this group of compounds.

The oxidations were made at room temperature, which varied from 18° to 22°.

Hydroxybenzoic Acids.

The first group studied was that of the hydroxybenzoic acids. Measurements were made on solutions to which neither acid nor alkali had been added. The results are given in tabular form. In this and the following tables the quantity of potassium permanganate, reduced by the organic substance, is expressed as cubic centimeters of solution. For the sake of convenience, the reduction is regarded as being complete, that is, to the manganous condition.

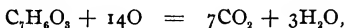
Table I.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, total volume 100 cc.

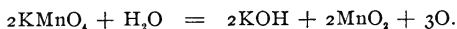
Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
1	. .	0.46	0.24
2	1.37	0.94	0.37
5	1.85	1.50	0.69
10	2.23	1.99	1.27
20	2.75	2.57	1.91
30	3.18	2.83	2.37
60	3.51	3.47	3.37
120	3.86	4.53	4.64
1080	5.50	6.00	6.22

Numerous other experiments were made, varying the quantity of substance, of potassium permanganate and of water. The general result was always the same, that is, the ortho compound was most readily oxidized, the para compound least readily. The differences were, in a few cases, greater than those tabulated above, but were of the same general character. The effect of a greater excess of permanganate is very slight, unless its concentration be increased.

Complete oxidation of the hydroxybenzoic acids according to the equation



would require for 0.005 of acid, 0.053 gram of potassium permanganate, yielding its oxygen according to the equation



The quantity of solution used, 15 cc., contained 60 milligrams of potassium permanganate.

A study was also made of the effect of the addition of varying amounts of acid or alkali to the solution. The results are brought together in Table II. The first column contains the number of equivalents of acid or alkali added to the solution. For example, the addition of 2 equivalents of acid or alkali means the addition of 1 molecule of sulphuric acid or 2 molecules of potassium hydroxide for every molecule of hydroxybenzoic acid in the solution.

Table II.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $\text{C}_7\text{H}_5\text{O}_3$, 15 cc. KMnO_4 , total volume 100 cc.

		KMnO ₄ reduced, cc.					
		Ortho.		Meta.		Para.	
		2 min.	5 min.	2 min.	5 min.	2 min.	5 min.
20 acid	.		5.40	.	5.80	.	4.99
4 "	4.57		5.04	.	5.27	.	2.89
2 "	3.47		3.90	.	4.00	.	1.93
0 "	1.37		1.85	0.94	1.50	0.37	0.69
1 alkali	0.51		0.65	0.25	0.40	0.20	0.37
2 "	0.17		0.50	3.65	4.07	1.79	2.99
4 "	0.63		1.35	3.90	4.28	1.62	2.87
10 "	1.70		.	3.53	.	1.22	.
20 "	2.36		3.05	3.30	3.96	1.15	1.59

In order to determine whether the effect of the addition of potassium hydroxide depends on the actual quantity of alkali in the solution, or on its concentration, measurements were made on solutions diluted with varying quantities of water. In the following table the figures at the head of the columns refer to the total volume of the solution.

Table III.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, time 2 minutes.

	KMnO ₄ reduced, cc.				
	Ortho.		Meta.		
	50 cc	100 cc.	50 cc.	100 cc.	150 cc.
1 acid	3.07
0 "	2.34	1.37	1.96	0.94	0.37
1 alkali	1.44	0.51	4.16	0.25	0.14
2 "	1.63	0.17	4.34	3.65	0.24
4 "	1.89	0.63	4.43	3.90	3.20
6 "	2.23	. .	4.42
10 "	. .	1.70	. .	3.53	. .
12 "	2.84
20 "	. .	2.36	. .	3.30	2.61

A careful study of these results leads to the conclusion that the effect of the alkali depends on its concentration in the solution, and not on the actual quantity present. For example, in the first column the point of minimum oxidation corresponds to the presence of a carboxyl salt, while in the second column the same point is reached only when sufficient alkali is present to form a neutral salt.

By separate experiments it was shown that sodium hydroxide has exactly the same effect as potassium hydroxide, and that the presence of corresponding quantities of potassium or sodium chloride has no influence whatever on the rate of oxidation.

During the process of oxidation the solution becomes alkaline, unless the potassium hydroxide, formed by the reduction of the potassium permanganate, is neutralized by acid oxidation products of the organic substance. It was found that considerable quantities of oxalic acid are formed when salicylic acid is oxidized by potassium permanganate. Acetic acid is known to be a frequent oxidation product of aromatic compounds. In view of the uncertainty arising from these facts, and also from a consideration of the results presented in Table II., it seemed more satisfactory to start with solutions made alkaline by the addition of considerable quantities of potassium

hydroxide. Table IV. contains the results obtained by oxidation in alkaline solution.

Table IV.—Oxidation of Hydroxybenzoic Acids.

0.005 gram $C_7H_6O_3$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
2	1.70	3.53	1.22
10	3.25	4.70	2.39
30	4.66	5.25	3.93
60	5.34	5.50	5.02

Aminobenzoic Acids.

Table V.—Oxidation of Aminobenzoic Acids.

0.005 gram $C_7H_7O_2N$, 15 cc. $KMnO_4$, total volume 100 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
0.5 (at 0°)	1.35	1.24	0.73
1	2.18	2.26	1.59
2	2.41	2.73	1.92
15	2.81	3.67	3.47
340	3.58	4.89	4.89

The first three measurements were made at 0° because the experiments with the hydroxybenzoic acids show that the ortho compound is most readily oxidized in the first stages of the oxidation. These results with the aminobenzoic acids are exactly analogous to those obtained with the hydroxybenzoic acids. Further measurements were made in alkaline solution.

Table VI.—Oxidation of Aminobenzoic Acids.

0.005 gram $C_7H_7O_2N$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
2	1.90	2.78	1.12
10	3.33	4.67	2.29
30	4.91	6.17	4.28
60	5.94	6.75	4.88

Here also, as with the hydroxybenzoic acids, the order of velocities is, meta, ortho, para.

Berkeley¹ found that the rate of reduction of the nitrobenzoic acids by stannous chloride increases from the meta to the para compound. His results seem to harmonize very satisfactorily with the conclusions reached in the present investigation.

Nitrophenols.

The nitrophenols being easily obtained, experiments were tried with them.

Table VII.—Oxidation of Nitrophenols.

0.005 gram $C_6H_5O_3N$, 15 cc. $KMnO_4$, total volume 25 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
1	1.05	0.78	0.36
5	2.25	1.75	0.68
30	5.60	5.15	3.01

Table VIII.—Oxidation of Nitrophenols.

0.005 gram $C_6H_5O_3N$, 20 cc. $KMnO_4$, total volume 30 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
90	6.24	6.20	5.90
390	6.80	6.51	6.72

Table IX.—Oxidation of Nitrophenols.

0.05 gram $C_6H_5O_3N$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 50 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
10	0.42	1.84	0.30
30	1.12	3.27	0.35
60	1.51	4.33	0.69
120	2.15	4.67	0.91

The results with solutions of the free nitrophenols are similar to those obtained for the two preceding groups. Here also, in alkaline solution, the order of velocities is meta, ortho, para.

¹ Dissertation, Johns Hopkins University, 1899.

*Nitranilines.**Table X.—Oxidation of Nitranilines.*0.005 gram $C_6H_4O_2N_2$, 15 cc. $KMnO_4$, total volume 25 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
10	0.22	2.94	0.22
60	0.91	4.04	0.43
10 (at 100°)	5.08	5.82	3.15

*Table XI.—Oxidation of Nitranilines.*0.005 gram $C_6H_4O_2N_2$, 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 35 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
30	1.12	4.23	0.84
60	1.35	4.52	0.89
120	2.53	4.91	1.22
360	3.02	5.19	1.71

Both of these tables show the same order in the rates of oxidation of the nitranilines, namely, meta, ortho, para.

*Toluidines.**Table XII.—Oxidation of the Toluidines.*0.005 gram C_7H_9N , 15 cc. $KMnO_4$, 10 equivalents KOH, total volume 100 cc.

Time in minutes.	$KMnO_4$ reduced, cc.		
	Ortho.	Meta.	Para.
0.5	3.94	4.28	2.55
1	4.28	4.75	2.72
2	4.69	5.13	3.03
5	5.30	5.61	3.51

In acid solution the oxidation was rapid and nearly equal for all 3 isomers.

In all 5 groups a uniformity is shown only in alkaline solution. The differences in the rates of oxidation of isomeric

substances are quite marked and the rate of oxidation decreases from the meta to the para compound.

JOHNS HOPKINS UNIVERSITY,
June, 1905.

ORTHOSULPHAMINEBENZOIC ACID AND RELATED COMPOUNDS.

BY HAMILTON BRADSHAW.

A few years ago F. D. Wilson, working in the laboratory of the Johns Hopkins University, made a comparative study of orthosulphaminebenzoic acid, $C_6H_4 \begin{matrix} \nearrow COOH \\ \searrow SO_2NH_2 \end{matrix}$, and orthocarbaminebenzenesulphonic acid, $C_6H_4 \begin{matrix} \nearrow CONH_2^1 \\ \searrow SO_2OH \end{matrix}$. As a few points were left unsettled I have continued the work at the suggestion of President Remsen.

Wilson states that orthosulphaminebenzoic acid crystallizes in two forms, plates and needles, and that the quantity of alkali used in the hydrolysis of the benzoic sulphinide determines which form the acid will take on crystallization. Several experiments were made to test this point. Wilson boiled a solution of 20 grams of benzoic sulphinide with 15 grams of sodium hydroxide, in 500 cc. of water, until hydrolysis was complete. The solution was acidified and allowed to stand over night. Large, monoclinic crystals were deposited. In repeating this work it was found that complete hydrolysis was not reached even after 15 hours' boiling. After cooling and filtering, the solution was acidified with hydrochloric acid. Only needles were deposited. Another alkaline solution, obtained in exactly the same way, was divided into two portions. One part of it was acidified and allowed to stand. Both forms of crystals began to appear, but on agitating the solution the plates ceased to form and the acid came down in needles. The second portion was acidified and seeded with plate crystals. All of the acid was deposited in the form of plates. In an-

¹ THIS JOURNAL, 30, 353 and Dissertation.

other experiment Wilson used 10 grams of benzoic sulphinide to 20 grams of sodium hydroxide and 250 cc. of water. This solution, treated in the same way as the previous one, gave only needles, the yield being almost quantitative. In the first experiment in which these proportions were used, Wilson's conclusions were confirmed, that is, only needles were obtained. In the second, a few plate crystals formed among the needles. Moreover, it was found that this proportion of alkali caused complete hydrolysis in less than 3 hours.

To determine whether the presence of benzoic sulphinide would induce the formation of plate crystals, the next solution of the hydrolyzed benzoic sulphinide was divided into two portions. To one, benzoic sulphinide was added until the solution tasted sweet. When acidified, the solution deposited most of the acid in needles, only a few plates being formed. The second portion of solution, containing no benzoic sulphinide, yielded only large plate crystals. From these experiments it is evident that the form of the crystals does not depend on the quantity of alkali used, nor on the presence of benzoic sulphinide. It is very probable that the plate crystals are formed only when the acidified solution suffers the least possible disturbance. Similar relations are known to hold with many other substances.

As stated by Wilson, the plate form of the acid contains no water of crystallization, while the needle crystals lose 0.5 molecule of water of crystallization at 100° – 110° .

	Calculated for $C_6H_4(COOH)SO_2NH_2 \cdot \frac{1}{2}H_2O$.	I.	Found. II.
H_2O	4.29	4.33	4.25

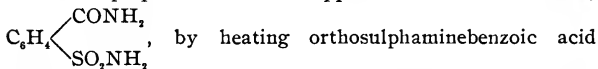
When crystallized from alcohol the acid is deposited in large rhombohedrons. Another form of crystals was obtained by hydrolyzing 20 grams of benzoic sulphinide with 30 grams of potassium hydroxide, in 500 cc. of water. When acidified, the solution deposited the acid in small, irregular crystals, about 1–2 mm. in diameter. The study of the crystalline form was not considered to be of sufficient importance to justify further investigation. The melting point of the acid, in whatever form it may be crystallized, is 152° (uncorr.).

Orthosulphaminebenzoic acid loses water when heated and is converted, at least partially, into benzoic sulphinide. A portion is probably converted into acid ammonium orthosulphobenzoate, as is the case with parabromorthosulphaminebenzoic acid.¹ Wilson states that in a rapid current of air the needles decompose at 115° , the plates at about 128° , and that, in a closed tube, the needles decompose at 145° , the plates at 135° .

In repeating this work, an apparatus was used similar to that described by Wilson, but the thermometer was placed in the glass tube with the boat, and windows of mica were fixed in the outer casing, to permit the reading of the thermometer and accurate observation of the decomposition. The crystals were powdered before being placed in the boat. It was found that both needles and plates became sweet when heated at 114° – 116° , for 2 hours, either in a rapid current of air or in a closed tube. Very little water collected in the cool part of the tube. Generally a slight sublimate of benzoic sulphinide was noticed.

Wilson's Diamide.

Wilson prepared what he supposed to be the diamide,



with ammonium thiocyanate. By following his directions carefully, a product was obtained which melted at 256° – 257° (uncorr.). Wilson gives 263° . It is very soluble in water, insoluble in cold alcohol, more soluble in hot alcohol. It gives off ammonia when treated in the cold with a solution of sodium hydroxide. These facts indicated that the substance is ammonium orthocarbaminebenzenesulphonate.² A determination of nitrogen completed the evidence :

0.2450 gram salt gave 0.0315 gram N.

	Calculated for $\text{C}_6\text{H}_4(\text{CONH}_2)\text{SO}_2\text{ONH}_4$.	Found.
N	12.86	12.85

¹Blanchard : *THIS JOURNAL*, 30, 509.

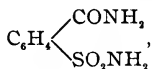
²Wilson : *Loc. cit.*, p. 370.

Orthocarbaminebenzenesulphonic Acid.

Potassium orthocarbaminebenzenesulphonate was prepared as directed by Wilson. When this salt is heated with phosphorus oxychloride, a compound is obtained which Wilson supposed to be orthocarbaminebenzenesulphone chloride. He crystallized it from chloroform and found the melting point to be 63° . By the action of phosphorus pentachloride on the same salt, Sohon¹ obtained orthocyanbenzenesulphone chloride, which he identified by converting it into orthocyanbenzenesulphonic acid. It seemed very probable that the reaction with phosphorus oxychloride would give the same product. The chloride was prepared as directed by Wilson, and crystallized from chloroform. It melts at 69° – 70° (uncorr.). The same substance was then prepared by the action of phosphorus oxychloride on potassium orthocyanbenzenesulphonate. This salt was obtained from the ammonium salt which is formed by the action of ammonia on the unsymmetrical chloride of orthosulphobenzoic acid.² The chloride obtained in this way melted at 69° – 70° . Jesurun³ prepared the same chloride by heating benzoic sulphinide with 2 molecules of phosphorus pentachloride, in a sealed tube, at 70° – 75° . He gives the melting point as 69° – 70° . Specimens of the chloride prepared by all three of these methods were found to have the same melting point, 69° – 70° , which was not lowered by mixing one specimen with another. There is no doubt, therefore, that the action of phosphorus oxychloride includes dehydration of the carbamide group,



This explains Wilson's failure to obtain the diamide,



by the action of ammonia on the chloride which he supposed to be orthocarbaminebenzenesulphone chloride. Jesurun⁴ de-

¹ THIS JOURNAL, 20, 271.

² *Ibid.*, 30, 268.

³ Ber. d. chem. Ges., 26, 2288.

⁴ *Ibid.*, 26, 2296.

scribes the action of ammonia on orthocyanbenzenesulphone chloride as follows: If an excess of ammonia is used the

product is pseudosaccharin amide, $C_6H_4 \begin{matrix} \diagup C(NH_2)_2 \\ \diagdown SO_2 \end{matrix} \diagup N$, melt-

ing above 300° . If the chloride is treated with benzene, in which the theoretical quantity of ammonia has been dissolved,

the product is orthocyanbenzenesulphonamide, $C_6H_4 \begin{matrix} \diagup CN \\ \diagdown SO_2NH_2 \end{matrix}$,

melting above 260° . This work was repeated, using the chloride obtained by Wilson's method, and Jesurun's results were confirmed, except in regard to the melting points. Pseudosaccharin amide, when crystallized from hot water, melts at 297° (uncorr.). Analyses:

I. 0.2025 gram substance gave 0.0310 gram N.

II. 0.1722 gram substance gave 0.0267 gram N.

III. 0.2118 gram substance gave 0.2712 gram $BaSO_4$.

	Calculated for $C_6H_4 \begin{matrix} \diagup C(NH_2)_2 \\ \diagdown SO_2 \end{matrix} \diagup N$.	Found.	
		I.	II.
N	15.38	15.30	15.49
S	17.59	. .	17.60

Orthocyanbenzenesulphonamide melts at 160° (uncorr.), changing completely, at its melting point, to the isomeric substance, pseudosaccharin amide, which melts at 297° (uncorr.). If heated rapidly no melting is observed at 160° . This explains Jesurun's observation that the substance melts above 260° .

When orthocyanbenzenesulphonamide is heated with a dilute solution of sodium hydroxide it is converted into benzoic sulphinide. It may be that the diamide is first formed and loses ammonia immediately. The diamide has not yet been prepared.

Anilineorthosulphonic Acid.

This acid can be prepared by the action of sodium hypobromite on an alkaline solution of potassium orthocarbaminebenzenesulphonate. Forty grams of this salt and 32 grams of

sodium hydroxide were dissolved in 320 cc. of water. The solution was warmed to 80° on the water-bath, and 28 grams of bromine, dissolved in 220 cc. of a 10 per cent solution of sodium hydroxide, were added drop by drop. The mixture was heated about 15 minutes and, after cooling, was acidified with hydrochloric acid. By evaporating to a very small bulk and filtering while hot, the sodium chloride was removed. The anilineorthosulphonic acid crystallized out on cooling and was obtained pure by recrystallization from hot water. Analysis :

0.0927 gram substance gave 0.1255 gram BaSO₄.

	Calculated for C ₆ H ₄ (NH ₂)SO ₂ OH.	Found.
S	18.51	18.58

If the sodium hypobromite is added rapidly to a cold solution of the carbamide, the chief product is tribromaniline. This is easily explained by the fact that anilineorthosulphonic acid is readily converted into tribromaniline by the action of free bromine.¹ If the sodium hypobromite is added slowly to a cold solution of the carbamide, the product is parabromanilineorthosulphonic acid. Even under the most favorable conditions some of this acid is formed. It is very insoluble in cold water and can be removed by filtration.

JOHNS HOPKINS UNIVERSITY,
June, 1905.

SOME DERIVATIVES OF PHENYLGLYCOCOLLORTHOSULPHONIC ACID.

BY HAMILTON BRADSHAW.

Anilineorthosulphonic Acid.

The preparation of this acid from orthocarbaminebenzenesulphonic acid has been described in the preceding article. This method, including the preparation of the carbamine acid, was too laborious for the production of the acid in any considerable quantity, and the method of Kreis² was tried, with good results. Acetanilide was brominated in glacial acetic acid

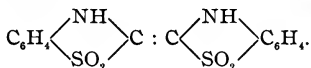
¹ Berndsen and Limpricht : *Ann. Chem. (Liebig)*, **177**, 100 (1875).

² *Ann. Chem. (Liebig)*, **286**, 377.

solution¹ and the product was crystallized from alcohol. The directions of Kreis were followed in the sulphonation of the parabromacetanilide. There was considerable charring and the yield was never better than 65 per cent of the theoretical. Any unchanged parabromaniline was removed by distilling an alkaline solution with steam. The bromine was removed by boiling with zinc dust and alkali.² Prolonged boiling was found to be necessary. After removing the zinc, the sulphonic acid was separated from the sodium chloride as described in the preceding paper. The identity of the substance was positively confirmed by diazotization and conversion into orthoethoxybenzenesulphonamide, $C_6H_4(OC_2H_5)SO_2NH_2$, melting at 156° (uncorr.).³ On titration, 0.9 gram of the acid required 0.2914 gram of potassium hydroxide for neutralization, calculated 0.3919 gram.

Phenylglycocollorthosulphonic Acid.

It was desired to prepare a sulphonic acid corresponding to phenylglycocollorthocarboxylic acid and to condense it to a compound analogous to indigo, thus :



Attempts were made to condense anilineorthosulphonic acid with chloracetic acid, just as anthranilic acid condenses with chloracetic acid.⁴ The proportions used correspond to those recommended for anthranilic acid. Ten grams of anilineorthosulphonic acid, 6.5 grams of chloracetic acid and 10.5 grams of sodium carbonate were dissolved in 320 cc. of water and the solution boiled for several hours, under a return condenser. The original acid was recovered unchanged. The same result was obtained when no sodium carbonate was added. The two acids were then heated, in aqueous solution, in a sealed tube,

¹ Hübner : Ann. Chem. (Liebig), 209, 355.

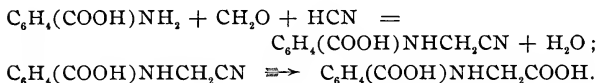
² Kreis : Loc. cit. Gerilowsky : Ber. d. chem. Ges., 29, 1075.

³ Franklin : THIS JOURNAL, 20, 462.

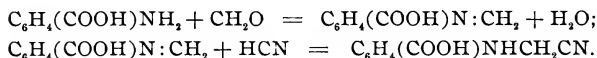
⁴ Mauthner and Suida : Monats. Chem., 9, 728. Heumann : Ber. d. chem. Ges., 23, 3432. German Imp. Pat., 56, 273.

with and without the addition of sodium carbonate, at about 150° , for several hours. No evidence of condensation was detected. Bromacetic acid was then tried, with the same negative result. Similar attempts to condense sulphanilic acid with chloracetic acid also failed. Anthranilic acid condenses very readily. Orthonitraniline does not condense with chloracetic acid, but condenses readily with bromacetic acid.¹ The failure of the anilinesulphonic acids to condense with chloracetic acid is probably to be explained by the strongly negative character of the sulphonic acid group.

Phenylglycocollorthocarboxylic acid is easily prepared by the action of formic aldehyde and hydrocyanic acid on anthranilic acid, and hydrolysis of the resulting nitrile:²



There are two steps in the first process, the condensation with formic aldehyde and the subsequent addition of hydrocyanic acid, thus:



This method was found to be very satisfactory when applied to anilineorthosulphonic acid. The following proportions were found to give the best results: Aniline-orthosulphonic acid, 8.65 grams, was dissolved in 50 cc. of hot water containing 3.25 grams of anhydrous potassium carbonate. Ten cc. of hydrochloric acid, sp. gr. 1.16 = 7.3 grams of HCl, were added, and then a concentrated solution of potassium cyanide, till the mixture became neutral to Congo red paper. It was now made slightly acid by means of a few drops of concentrated hydrochloric acid, whereupon 3.75 cc. of a 40 per cent solution of formic aldehyde were added and the mixture was warmed on the water-bath for about an hour. At the end of this time a concentrated solution of about 8 grams of potas-

¹ Plöchl: Ber. d. chem. Ges., 19, 7.

² German Imp. Pat., 117, 924; 120, 105.

see
data
1.590

sium hydroxide was added and the solution was boiled until evolution of ammonia ceased. After cooling, enough hydrochloric acid was added to precipitate the phenylglycocollorthosulphonic acid as the acid potassium salt, which is rather sparingly soluble in cold water. It dissolves in concentrated hydrochloric acid and the free sulphonic acid crystallizes out of the solution.

The materials from which this salt was obtained being comparatively difficult to prepare, most of the following experiments were made with parabromphenylglycocollorthosulphonic acid. This was prepared in exactly the same way as the bromine-free compound, 12.6 grams of parabromanilineorthosulphonic acid being substituted for the 8.65 grams of anilineorthosulphonic acid. The acid potassium salt obtained in this way is very insoluble in cold water. It was recrystallized from hot water, from which it is deposited in needles. The salt contains water of crystallization, but loses it in varying amounts when dried in the air. A determination of potassium was made on a portion dried at 125°.

0.2932 gram salt gave 0.0722 gram K_2SO_4 .

K	Calculated for	Found.
	$C_6H_5Br(SO_2OK)NHCH_2COOH.$	
	11.24	11.05

When a solution of this salt, in hot water, is rendered strongly acid with hydrochloric acid and allowed to cool slowly, the free sulphonic acid is deposited in flaky crystals. It is very soluble in water, much less soluble in a rather concentrated solution of hydrochloric acid. When titrated, 0.1119 gram required 0.0287 gram of sodium hydroxide for neutralization, calculated 0.0289 gram.

If the free acid, contaminated with potassium chloride, is dissolved in hot, absolute methyl alcohol, the solution filtered and evaporated to a rather small bulk, the acid is changed to an ester acid, which can be precipitated by the addition of ether. Analysis:

0.5841 gram substance gave 0.3369 gram AgBr.

	Calculated for $C_6H_5Br(SO_3OH)NHCH_2COOCH_3$.	Found.
Br	24.66	24.54

When titrated, 0.1708 gram of the ester acid required 0.0215 gram of sodium hydroxide for neutralization, calculated 0.0211 gram. The ester was saponified by boiling with an excess of a standard solution of sodium hydroxide. By titrating the excess of alkali, the amount consumed was determined. Total sodium hydroxide used for saponification and neutralization 0.0429 gram, calculated 0.0422 gram.

Attempts at Condensation.

1. Phenylglycocolloorthocarboxylic acid is converted into indigo by fusing with sodium hydroxide at 250° – 300° , dissolving the resulting mass in water and passing air through the solution.¹ Since fused alkali at this high temperature replaces the sulphonie acid group by phenolic hydroxyl, this method of condensation was not tried on parabromphenylglycocolloorthosulphonie acid.

2. Phenylglycocollo is converted into indigodisulphonie acid by the action of fuming sulphuric acid.² Phenylglycocolloorthocarboxylic acid gives no indigo by this method, but it seemed desirable to try it on the corresponding sulphonie acid. Accordingly, 15 grams of acid potassium parabromphenylglycocolloorthosulphonate were added, slowly, to 50 grams of fuming sulphuric acid, containing 20 per cent free sulphuric anhydride, the temperature being maintained below 40° . A considerable quantity of gas was evolved during the process of solution. The mixture was added to 100 grams of fuming sulphuric acid containing 80 per cent free sulphuric anhydride and allowed to stand for half an hour. The acid was then poured on ice. A white solid separated, which, on crystallization from hot water, was found to be parabromanilineorthosulphonie acid. Analysis :

0.5693 gram substance gave 0.4297 gram AgBr.

¹ Heumann : Ber. d. chem. Ges., **23**, 3432.

² Heumann : *Ibid.*, **24**, 1476, 3070. German Imp. Pat., **63**, 218 ; **68**, 372.

	Calculated for $C_6H_5Br(NH_2)SO_2OH$.	Found.
Br	32.11	31.71

0.3025 gram required 0.0478 gram sodium hydroxide for neutralization, calculated 0.0480 gram.

The fuming sulphuric acid removes the acetic acid portion of the molecule and probably oxidizes it to oxalic acid, which, of course, would appear as carbon monoxide and carbon dioxide. When phenylglycocollorthosulphonic acid is treated with fuming sulphuric acid it evolves gas just as the bromine derivative does.

3. Diacetyloxyl, $C_6H_5 \begin{matrix} \diagup N(C_2H_5O) \\ \diagdown C(OC_2H_5O) \end{matrix} \rangle CH$, is very easily

prepared by heating the neutral sodium salt of phenylglycocollorthocarboxylic acid with acetic anhydride.¹ Carbon dioxide is evolved during the reaction and the product is insoluble in water. It is easily converted into indigo by boiling with dilute alkali. This method of condensation was tried on parabromphenylglycocollorthosulphonic acid by boiling 5 grams of the acid potassium salt with 1.5 grams of anhydrous sodium acetate and 25 grams of acetic anhydride for some time, under a return condenser. No carbon dioxide was evolved during the reaction. The acetic anhydride was distilled off under reduced pressure. The residue was very soluble in water. The solubility of the product, and the fact that no carbon dioxide was evolved made it seem very probable that the substance obtained was still a sulphonic acid and that the reaction had not gone beyond the acetylation of the imino group.

4. The neutral esters of phenylglycocollorthocarboxylic acid are very easily converted into esters of indoxylic acid by the action of sodium alcoholates.² Attempts were made to prepare neutral esters of parabromphenylglycocollorthosulphonic acid by the action of methyl iodide on the silver salt of the acid methyl ester, and by the action of dimethyl sulphate on the neutral sodium salt of the acid, but without success. No

¹ German Imp. Pat., 113, 240.

² Vorländer and Schilling: *Ann. Chem. (Liebig)*, 301, 349.

further attempts were made in this direction, as the condensation probably depends on the presence of the carbonyl group, like all Claisen condensations.

5. Sodamide has been used recently in place of sodium hydroxide in the preparation of indoxyl and indoxylic acid from phenylglycocollorthocarboxylic acid.¹ The application of this method to the sulphonic acid gave some promise of success, because the temperature required is lower, and the disturbing influence of the fused alkali on the sulphonic acid group is practically eliminated. The sodamide was prepared by the method of Dennis and Browne.² No condensation product could be obtained, however, when acid potassium parabromophenylglycocollorthosulphonate was heated at about 200° with the sodamide, or at 250° with the sodamide diluted with potassium cyanide.

These methods, used in the preparation of indigo from phenylglycocollorthocarboxylic acid, having failed when applied to the corresponding sulphonic acid, further attempts to effect the condensation did not seem to be justified.

I desire to express my thanks to President Remsen for suggesting this problem to me.

JOHNS HOPKINS UNIVERSITY,
June, 1905.

ON DERIVATIVES OF FORMHYDROXAMIC ACID AND THE POSSIBLE EXISTENCE OF ESTERS OF FULMINIC ACID. II.

BY H. C. BIDDLE.

It was suggested some time ago by Nef³ that the esters of fulminic acid might result by the elimination of hydrogen chloride from the esters of chloroformyloxime (formylchloridoxime). In the preceding paper⁴ I discussed the synthesis and general properties of methylchloroformoxime and called attention to the peculiar isonitrile-like odor which is produced when a solution

¹ German Imp. Pat., 137, 955.

² J. Am. Chem. Soc., 26, 587.

³ Ann. Chem. (Liebig), 280, 340 (1894).

⁴ THIS JOURNAL, 33, 60 (1895).

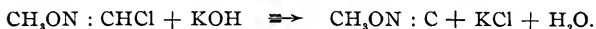
of this ester in ether or ligroin is treated with potassium hydroxide. It was thought at the time that the odor might be due to the formation of methyl fulminate.

As a continuation of the work has been somewhat retarded by the difficulty of securing material, the complete study of the reaction has only been recently effected.

The liquid remaining after evaporating the ether, or ligroin, was distilled under diminished pressure. From a preliminary analysis of the colorless distillate and a determination of its molecular weight, I was at first disposed to consider that I was dealing with the ester $(\text{CH}_3\text{ONC})_2$.

Subsequent study of the reaction, however, has shown that the substance under consideration was really methyl diimino-oxalate, $\text{HN} : \text{C}(\text{OCH}_3)\text{C}(\text{OCH}_3) : \text{NH}$, and that, in the action, of potassium hydroxide on methyl chloroformoxime, there is produced not only this body but also, among other products, methyl cyaniminocarbonate, $\text{HN} : \text{C}(\text{OCH}_3)\text{CN}$, and the potassium salts of hydrocyanic, cyanic and oxalic acids. It is evident that no molecular rearrangement of the molecule of methyl fulminate will account for these reaction products and it is equally evident that their occurrence points to the complete disruption of the molecule of methyl chloroformoxime.

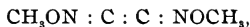
In an attempt to account for these unexpected results we may note that the primary action which we should naturally expect would be expressed by the simple equation :



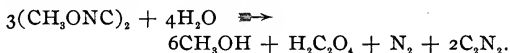
It is highly probable that the fulminic ester thus occurs as an intermediate product, but, if so, its instability under the conditions of the experiment evidently precludes its isolation.

If it were immediately dissociated we should naturally expect, as dissociation products, carbon monoxide or formic acid and methyl hydroxylamine. The presence of traces of potassium formate in the alkaline residue points to a slight dissociation in this direction.

On the other hand, the fulminic ester, being unsaturated, might condense to form the double molecule,

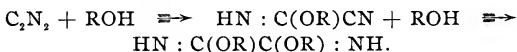


and this, in turn, suffering decomposition, might be dissociated simultaneously in two directions, in one case leading to the formation of oxalic acid and methyl alcohol, and in the other to the formation of cyanogen and methyl alcohol, according to the equation :



Such twofold dissociation of the double molecule fully accounts for the occurrence of salts of hydrocyanic, cyanic and oxalic acids. It might be urged that the oxalic acid arises from the decomposition of the diiminooxalic ester, but, as shown by Nef,¹ diiminooxalic esters, in the presence of an alkali, under no condition yield derivatives of oxalic acid. This was fully confirmed in the case of the methyl ester by allowing it to stand in contact with solid potassium hydroxide for 24 hours. Not a trace of potassium oxalate was formed.

The occurrence of methyl alcohol and cyanogen serves fully to explain the formation of both cyaniminocarbonic ester and diiminooxalic ester in the reaction. As shown by Nef,² cyanogen, in the presence of an alcohol and in contact with an alkali, absorbs 1 and 2 molecules of the former, giving rise to the esters just named,



Diiminooxalic methyl ester was synthesized and compared with the product obtained from the action of potassium hydroxide on methyl chloroformoxime. The methyl ester proved to be a crystalline solid, melting at $29^\circ.5$ – $30^\circ.5$. The product derived from methyl chloroformoxime was not obtained as a solid, but, as I shall show later, the failure to solidify was due to the presence of traces of cyaniminocarbonic ester, from which, with the small quantity at my command, 0.5 gram and less, it was found impossible to free it. As regards composi-

¹ Ann. Chem. (Liebig), 287, 284 (1895).

² Ibid., 287, 223.

tion, constitution and general behavior towards reagents, the two esters proved to be absolutely identical.

From these results it seems highly improbable that the carbyloxime esters will ever be synthesized by as drastic a method as that involved in the elimination of hydrogen chloride from the esters of chloroformoxime. The pronounced tendency of the entire molecule to undergo dissociation under the conditions obtaining in the reaction naturally indicates the futility of all synthetic methods in which this dissociative tendency is not greatly diminished.

EXPERIMENTAL.

Action of Potassium Hydroxide on Methyl Chloroformoxime.—To a well cooled solution of 10 grams of methyl chloroformoxime, in absolute ether, is added, gradually, an excess of powdered potassium hydroxide. There arises immediately the isonitrile-like odor already referred to in the previous paper. The action, slight at first, is later accompanied by the evolution of small quantities of an inert gas, possessing the general negative properties of nitrogen. During the entire reaction the liquid remains perfectly free from any odor of ammonia. As soon as the completion of the action is indicated by the disappearance of the chloride from the solution, the ether is decanted from potassium salts, evaporated and the brown liquid remaining, less than 1 gram, is distilled under diminished pressure. There is thus obtained approximately 0.5 gram of colorless liquid, boiling at about 60° (25 mm.). The small amount of product naturally precluded an exact determination of the boiling point.

The residue in the distilling bulb, fully 0.3 gram, is converted into a resin at a higher temperature.

The colorless liquid was redistilled and analyzed :

0.1248 gram substance gave 0.1910 gram CO₂ and 0.0796 gram H₂O.

0.0787 gram substance gave 16.5 cc. moist N₂ at 13° and 752.3 mm.

	Calculated for $C_4H_8O_2N_2$.	Found.
C	41.46	41.73
H	6.90	7.08
N	24.12	24.6

A determination of the molecular weight was made by the freezing-point method, using benzene as solvent.

0.1079 gram substance in 17.44 grams of benzene gave a depression of $0^{\circ}.285$.

0.1361 gram substance in 17.44 grams of benzene gave a depression of $0^{\circ}.360$.

	Calculated for $C_4H_8O_2N_2$.	I.	Found. II.
Mol. wt.	116	108.5	108.3

On treating the liquid with concentrated hydrochloric acid, it is saponified to methyl alcohol, ammonia and oxalic acid. Not a trace of methoxylamine or hydroxylamine is produced in this reaction.

Although not in a condition of absolute purity, the substance analyzed is, without doubt, methyl diiminooxalate. As will be shown later, its general properties fully identify it with this ester.

An examination of the mixture of salts resulting from the action of potassium hydroxide on methyl chloroformoxime showed the presence, in quantity, of potassium chloride, cyanide, cyanate, oxalate and carbonate, together with traces of potassium formate.

The cyanic acid was detected by the method suggested by Schneider.¹

For the complete identification of the methyl diiminooxalate obtained above, attention was now turned to the direct synthesis of this body.

Methyl Diiminooxalate, $HN : C(OCH_3)C(OCH_3) : NH$.—As shown by Nef,² the ethyl esters of cyaniminocarbonic acid and diiminooxalic acid are formed by conducting chlorine into a solution of potassium cyanide in water-alcohol, the course of the reaction, as he has indicated, being essentially as follows :

¹ Ber. d. chem. Ges., 28, 1540 (1895).

² Ann. Chem. (Liebig), 287, 296.

The cyanogen chloride produced is absorbed by potassium cyanide, forming the addition product, $\text{KNC}(\text{CN})\text{Cl}$, which is then converted by the alcohol into cyaniminocarbonic ester. Under the influence of the alkali a portion of the latter body adds a second molecule of alcohol, thereby giving rise to diminoxalic ester.

Since the methyl esters of cyaniminocarbonic acid and diminoxalic acid had not been prepared, they were synthesized according to the general method given by Nef.

A somewhat rapid stream of chlorine is run into a solution of 50 grams of potassium cyanide in 300 grams of water and 100 grams of methyl alcohol, cooled to -5° – 0° . As soon as the solution, which smells strongly of cyanogen chloride, becomes weakly alkaline or neutral, it is extracted with ether, the ether extract is washed 3 times with water to remove alcohol, and is then dried by calcium chloride. The brown oil remaining after distilling off the ether and cyanogen chloride, was fractionated under diminished pressure. It was thus separated into two parts, the larger portion boiling at 33° – 34° and the lesser at 54° – 55° (22 mm.) The latter soon solidified in the receiver to a mass of colorless, transparent plates.

The larger fraction, as shown by a nitrogen determination, is methyl cyaniminocarbonate,



0.12 gram substance gave 33.7 cc. moist N_2 at 12° and 757.7 mm.

	Calculated for $\text{C}_2\text{H}_4\text{ON}_2$.	Found.
N	33.33	33.31

Methyl cyaniminocarbonate is a colorless, mobile liquid, boiling at 33° – 34° (22 mm.). It possesses a peculiarly penetrating and irritating odor, somewhat resembling that of an isonitrile and practically identical with that noted during the early stages of the action of potassium hydroxide on methyl chloroformoxime. The substance is but slightly soluble in water. It cannot be kept for any length of time without undergoing marked decomposition.

Thus, if exposed to diffused sunlight for a few days, it is completely converted into a dark, resinous tar.

The smaller fraction, as shown by analysis, is methyl diiminooxalate, $\text{HN} : \text{C}(\text{OCH}_3)\text{C}(\text{OCH}_3) : \text{NH}$.

0.1593 gram substance gave 0.2418 gram CO_2 and 0.1000 gram H_2O .

0.0888 gram substance gave 18.4 cc. moist N_2 at 14° and 755.3 mm.

	Calculated for $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$.	Found.
C	41.46	41.38
H	6.90	6.97
N	24.12	24.30

Methyl diiminooxalate crystallizes in colorless, transparent plates, melting at $29^\circ.5$ – $30^\circ.5$. It is characterized by a peculiar, sweetish odor, which is always noticed on the completion of the action of potassium hydroxide on methyl chloroformoxime. The substance is more stable than methyl cyaniminocarbonate, although, on standing, it is gradually converted into a dark resin.

Like its homologue, the ethyl ester, concentrated hydrochloric acid saponifies the methyl ester to methyl alcohol, ammonia and oxalic acid. If added to an excess of well cooled, dilute hydrochloric acid, 1 con. acid : 10 water, it is resolved into ammonia and methyl oxalate. On extracting the solution with ether and evaporating the latter, the methyl ester separates in characteristic crystals, melting at 54° .

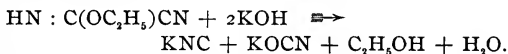
Methyl diiminooxalate, as synthesized above, proved to be identical in every respect with the product obtained by the action of potassium hydroxide on methyl chloroformoxime, save in the fact that the latter did not solidify. It can scarcely be questioned that this failure to solidify is due to the contaminating presence of a trace of cyaniminocarbonic ester, which could not be separated from the small amount of substance obtained, about 0.5 gram.

This appears not only from the fact that the product derived from methyl chloroformoxime indicated, by a variable boil-

ing point, the presence of a lower boiling liquid, but also from the fact that, in one instance, in which an excess of potassium hydroxide was avoided, the substance resulting possessed the properties, such as boiling point, odor, etc., not of the diimino-oxalic ester but of the cyaniminocarbonic ester.

It is evident, then, that in both syntheses, cyaniminocarbonic ester is first produced and that this, in the presence of the alkali, subsequently adds a molecule of alcohol to form the diimino-oxalic ester.

As shown by Nef,¹ so pronounced is the tendency of ethyl cyaniminocarbonate to add alcohol in the presence of an alkali, that the ester and alkali alone suffice to give rise to diimino-oxalic ester, the action depending on the partial decomposition, and the subsequent addition of the alcohol to unchanged cyaniminocarbonic ester:



The tendency of the methyl ester to absorb a molecule of alcohol is equally pronounced, as is shown by the following experiment:

A somewhat rapid stream of chlorine was run into a solution of 50 grams of potassium cyanide in 300 grams of water and 100 grams of methyl alcohol, cooled to -5° – 0° . As soon as the solution became neutral there was added to it a solution of 32 grams of potassium cyanide, in 50 grams each of methyl alcohol and water.

After standing for 6 hours, at 20° – 30° , the mixture was diluted slightly with water and extracted with ether, as in the previous experiment.

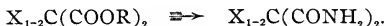
The reaction product consisted almost entirely of diimino-oxalic ester with a trace of cyaniminocarbonic ester.

¹ Ann. Chem. (Liebig), 287, 282.

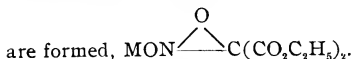
AMINE DERIVATIVES OF MESOXALIC ESTERS.

BY RICHARD SYDNEY CURTISS.

In a former paper¹ the fact was noticed that many ineffectual attempts, by various investigators, have been made to link one and two amine groups to the methylene carbon in malonic esters, to form $H_2NCH(COOR)_2$ and $(H_2N)_2C(CO_2R)_2$. A saponification was always first effected and an amine formed whenever ammonia was allowed to act on the haloid esters:



More recently Willstätter² has tried, unsuccessfully, to displace the two negative groups in ethyl bromnitromalonate, $NO_2CBr(CO_2C_2H_5)_2$, by the amino group, working with ammonia in alcohol, water and ether solutions. The bromine was eliminated and salts of the base with ethyl isonitromalonate



The first successful results recorded in this line of work were those obtained when negatively substituted ammonias (aniline, etc.) were used with brominated malonic esters. In this manner ethyl anilinomalonate, $C_6H_5NHCH(CO_2C_2H_5)_2$, and ethyl dianilinomalonate, $(C_6H_5NH)_2C(CO_2C_2H_5)_2$,³ as well as a series containing substituting groups in the benzene ring were made.⁴ The only aminomalonic ester containing an amine group relatively more positive than ammonia has recently been made by the action of dimethylamine on methyl dibrommalonate.⁵ This resulted in the formation of methyl tetramethyldiaminomalonate, $[(CH_3)_2N]_2C(CO_2CH_3)_2$. O. Piloty and J. Neresheimer⁶ have recently obtained ethyl aminomalonate.

¹ THIS JOURNAL, 19, 691.

² Ber. d. chem. Ges., 34, 1775.

³ THIS JOURNAL, 19, 693, 698.

⁴ Ibid., 30, 133.

⁵ Willstätter: Ber. d. chem. Ges., 35, 1378.

⁶ Ibid., 39, 514 (1906).

Some time ago,¹ while engaged in a study of the arylamine derivatives of ethyl malonate, the action of 2 molecules of aniline on a molecule of ethyl oxomalonate, $\text{OC}(\text{CO}_2\text{C}_2\text{H}_5)_2$, was tried. Heat was generated on mixing the substances and, after 24 hours, balls of long, prismatic crystals were found in the oil. This substance melted at 117° – 118° (uncorr.), and agreed in this and other characteristics with ethyl dianilinomalonate, $(\text{C}_6\text{H}_5\text{NH})_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, the product which is formed by the action of aniline on ethyl dibrommalonate.² This result, however, was not published at the time. Subsequently, Conrad and Reinbach³ described the reactions between these two substances using, however, the free acid instead of its ester. They obtained dianilinomalonic acid from the aniline salt first produced and suggest that the esters may be so formed by the action of aniline on ethyl and methyl oxomalonate. Schmitt⁴ has recently tried this reaction. His product of the action of aniline on ethyl mesoxalate called "bisanilide de mesoxalate d'ethyle" must be very impure, however, as he gives its melting point as 103° , whereas it really melts at 117° – 118° (uncorr.), when pure.

In like manner he has prepared methyl dianilinomalonate and gives its melting point as $113^\circ.5$. Conrad and Reinbach,⁵ who first made this substance, found that it melted 11° higher, viz., at 125° . No analytical figures accompany Schmitt's work. He has, apparently, overlooked both papers in which the properties of these two substances are described.

Petrieve⁷ studied the effect of an aqueous solution of ammonia on ethyl dihydroxymalonate. He obtained "yellow deliquescent crystals" of dihydroxymalonamide, $(\text{HO})_2\text{C}(\text{CONH}_2)_2$. The ester was, therefore, saponified. I have succeeded in getting an action with dry ammonia gas on the ketone group in ethyl oxomalonate, $\text{OC}(\text{CO}_2\text{C}_2\text{H}_5)_2$, forming an unstable, addition

¹ THIS JOURNAL, 19, 701.

² *Ibid.*, 19, 695.

³ Ber. d. chem. Ges., 35, 1820.

⁴ Compt. rend., 141, 49.

⁵ THIS JOURNAL, 19, 695.

⁶ *Loc. cit.*

⁷ J. russ. Chem. Ges., 10, 76. Beilstein: "Handbuch d. Org. Chem.," I, 1398.

product, $\text{HN} \begin{cases} \text{COH}(\text{CO}_2\text{C}_2\text{H}_5)_2 \\ \text{COH}(\text{CO}_2\text{C}_2\text{H}_5)_2 \end{cases}$, while leaving intact the usually reactive ester part of the molecule.

The Action of Ammonia on Ethyl Dihydroxymalonate.

When studying the action of ammonia gas on ethyl dihydroxymalonate it was noticed that the results vary greatly with the conditions of the experiment. To obtain a fairly pure product a low temperature is necessary, as well as a properly chosen solvent and drier. Seven and six-tenths grams of pure ethyl dihydroxymalonate were dissolved in 120 cc. of dry benzene. To remove the water formed in the reaction about 70 grams of zinc chloride, in small sticks, were added, and immediately thereafter, ammonia gas, carefully dried over sticks of potassium hydroxide, was passed into this solution. The whole was kept at the freezing point of the solvent. Care was also taken to avoid atmospheric moisture entering the apparatus. After a few seconds the clear, colorless solution becomes cloudy, due to the separation of water. After 20 minutes this begins to disappear and in 2 minutes more the solution is again water-clear and the action is over. The increase in weight of the mass is about 3 grams. Toward the end of the operation a faint tint of yellow appears, due to an oily impurity which is very difficult to remove. If the operation is carried out at ordinary room temperatures this is largely increased. The solution is now allowed to stand for 10 minutes in the freezing mixture and then filtered from the encrusted zinc chloride. The benzene is removed from the clear filtrate by distillation from a water-bath at 50° (80 mm.); 6.8 grams of a yellowish-white, crystalline mass remain in the distilling flask. This was at once dissolved in 125 cc. of warm, dry ether and filtered from a little yellowish-white impurity. The solution was cooled in ice-water, and the crystals which separated on standing 15–20 minutes were filtered off. The ethereal filtrate is slightly opalescent. The formation of the substance which causes this increases slowly, hour by hour, in the solution, so

that it is necessary to crystallize quickly and avoid the moisture of the air coming in contact with the substance.

The new compound was recrystallized once or twice from dry ether, until the melting-point showed no change. It melts at 103° – 105° on quickly heating; the melting point is not sharp, as it commences to decompose as soon as superficially melted. The colorless oil at first formed instantly begins to turn amber-yellow while giving off a colorless gas. If melted in a test tube, ammonia is given off in quantity at 105° – 110° .

Analysis of the substance, recrystallized from dry ether and dried in a vacuum over solid potassium hydroxide :

I. 0.2494 gram substance gave 9.5 cc. N at 25° and 736.4 mm.

II. 0.2976 gram substance gave 10.2 cc. N at 24° and 756.3 mm.

III. 0.2252 gram substance gave 0.3832 gram CO_2 , and 0.1237 gram H_2O .

Calculated for $\text{HN} \begin{cases} \text{COH}(\text{CO}_2\text{C}_2\text{H}_5)_2 \\ \text{COH}(\text{CO}_2\text{C}_2\text{H}_5)_2 \end{cases}$		Found.		
		I.	II.	III.
C	46.02	46.35
H	6.30	6.08
N	3.84	4.26	4.03	. .

The substance is ethyl dihydroxyiminodimalonate and appears to be formed by the substitution of the imine group in place of two hydroxyl groups in 2 molecules of ethyl dihydroxymalonate, $(\text{HO})_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, or by direct addition of ammonia to the keto group in ethyl oxomalonate, from which it can also be made. It crystallizes from ether in flat, rectangular tablets; if the solution be poured on a watch-glass, in beautiful, large, fern-like sprays. It is very easily electrified when rubbed with glass. It is insoluble in carbon bisulphide, slightly soluble in ligroin. It dissolves fairly well in ether, easily in benzene and acetic ether, very easily in acetone and chloroform. It is insoluble, as such, in cold water, but is, however, quickly decomposed by it. The solution in water smells strongly of ammonia and gives, on evaporation in a vacuum, ethyl dihydroxymalonate, m. p. 57° . It is dis-

sociated in the same manner, though more slowly, by standing in moist air, and also by solution in alcohol. It can be kept, when pure, in a desiccator over solid potassium hydroxide for weeks, without losing ammonia.

Phosphorus pentachloride (1. mol.), mixed with the crystals, generates heat and soon causes a semi solution, evolving large quantities of hydrogen chloride. The resulting product has not been fully investigated.

The study of the reactions of mesoxalic esters with ammonia derivatives and hydrazines will be continued.

URBANA, ILL.,
Feb. 24, 1906.

REPORTS.

The Oxidation of Atmospheric Nitrogen with Reference to the Manufacture of Nitrates and Nitric Acid.

(1) Die Nutzbarmachung des Luftstickstoffs. Rede, gehalten bei der Eröffnung des neuen technisch-chemischen Instituts der Königlichen technischen Hochschule zu Berlin, am 25ten November, 1905, Von dem Director des Instituts, Geheimer, Regierungsrat Prof. Dr. Otto N. Witt.¹

(2) Ueber die Oxydation des Stickstoffes in der Hochspannungs-flamme. Von Johannes Brode, Ph.D., Privatdozent für physikalische Chemie und Electrochemie an der Technischen Hochschule zu Karlsruhe, Baden. Halle: Wilhelm Knapp. 1905. 63 pp. Price, M. 2.50.

Prof. Witt's speech and Dr. Brode's monograph together cover the subject; the former is a popular description of the Birkeland-Eyde process, is illustrated by diagrams and photographs, and may be considered authoritative, as the inventors were present. The latter goes deeper into the subject of nitrogen oxidation, and includes investigations of high-tension flames by Brode and by others, giving, also, minuter details of the technical processes than does Witt.

We owe the first experiments on the oxidation of atmospheric nitrogen to Cavendish,² who, in 1781, noticed that the water formed by burning hydrogen in an excess of air contains nitric acid, and in 1786³ showed that all of the nitrogen in a volume of air can be burned if enough oxygen is added and

¹ Chem. Indus., 28, 699, 1905.

² Thorpe: "Essays in Historical Chemistry," p. 83.

³ Phil. Trans., 75, 372.

energy enough supplied in the form of electric sparks; a small bubble of gas always remained unburned, as Cavendish observed, which bubble Rayleigh,¹ repeating the experiment 100 years later, showed to be argon. Priestley made observations similar to those of Cavendish at about the same time.² Spottiswoode,³ in 1880, found that, under certain conditions, the discharge of an alternating current with high potential, in air, is not in the form of sparks or of an arc, but has the form of a perfect flame. Subsequent attempts to utilize the Cavendish reaction have little technical or scientific interest till 1895, when Naville and Guye⁴ showed that where there is a certain concentration of nitrous gases in contact with the sparks, the ratio of oxidation to energy employed lessens greatly; hence, oxidized air should be instantly removed from the sparking space; it must not be passed through again, and the sparking chamber should be as small as possible, to hinder diffusion of oxidized air into the fresh air entering. In the same year Lord Rayleigh and Sir William Ramsay discovered argon, and Rayleigh,⁵ repeating the Cavendish experiment, determined the ratio of energy used to nitric acid obtained. As his aim was to isolate argon, he used a mixture of 1 vol. of nitrogen and 2 vols. of oxygen. From this mixture he obtained 49 grams of HNO_3 per kilowatt hour.⁶ Rayleigh's work led Dougall and Howles⁷ to a careful study of methods of increasing the yield. They employed an alternating current of 60 periods per second, with varied resistance. Their most important discovery was that, with a given potential, the ratio of acid formed to current employed falls as the current increases. Their best yield from the Rayleigh nitrogen-oxygen mixture was 65 grams of nitric acid, and from air 33.6 grams of nitric acid per kilowatt hour, with 0.15 ampere current, 60 periods per second and 8,000 volts potential, while with 0.3 ampere about half the relative amount of acid was obtained. Their work was confirmed and enlarged by DeKowalski and Moseicki,⁸ who showed that the yield of acid can be increased by using a rapid alternating current. With a current of 0.05 ampere, 6,000 to 10,000 periods per second and a tension of 50,000 volts, they obtained 55 grams HNO_3 per kilowatt hour from air.

¹ Phil. Trans., 186, 197.

² *Ibid.*, 78, 473.

³ P. Roy. Soc., 30, 174.

⁴ German Patent, No. 88,320.

⁵ Phil. Trans., 186, 197.

⁶ In this report the weight of nitric acid— HNO_3 —per kilowatt hour, calculated from the amount of nitrogen oxidized, is used as relative measurement. It must not be understood that concentrated nitric acid was actually made.

⁷ Manchester Memoirs, 44, 1; Various patents.

⁸ Société internationale des Electriciens, 2 Serie, III., No. 26. *Electrotechnische Zeit.*, 1904, p. 27.

Bradley and Lovejoy's¹ patent was exploited by the Atmospheric Products Co., with works at Niagara Falls. For the continuous arc of weak intensity used by Rayleigh, Dougall and de Kowalski, these two later inventors raised the yield of acid by substituting arcs quickly torn away from the electrodes, thus giving a rapid series of isolated sparks or arcs. Their apparatus is illustrated in Fig. I. A rotating vertical axis car-

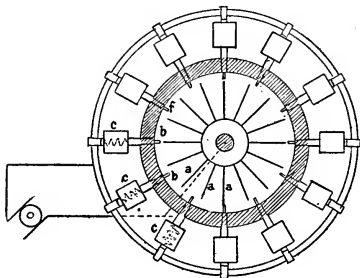


Fig. I.

ries a circle of electrodes *a*, projecting from the axis at a right angle to it. Opposite to them, on the periphery of a circle, are a number of electrodes *b*, each connected with induction coils *c*; as the axis rotates, a moving electrode approaches a fixed electrode and an arc forms, which tears off as the axis rotates, but, in the interval, other electrodes have approached, forming new arcs. The resistance of the induction coil causes a sudden expenditure of energy at the instant the arc is torn away, with resulting high temperature; as, in the next instant, no heat is generated at this point, sudden, extreme cooling occurs. Their maximum yield was 88 grams of nitric acid per kilowatt hour. They used direct current and 10,000 volts tension. Work stopped in the summer of 1904.

Before further consideration of the technical processes, let us turn to the theory of the oxidation, as stated by Dr. Brode. When air is heated to about 2000° or higher, nitrous gases are formed, no matter whether the high temperature is attained chemically, by burning hydrogen, magnesium, etc., or physically, using electric arcs and sparks, or higher resistance. Therefore, the conditions of oxidation are neither chemical nor electrical, but simply thermal. When the nitrous gases thus formed are shaken with water, a mixture of nitric and nitrous

¹ *Electrochem. Ind.*, 1, 20, 100, 386. Cf. various patents.

acids is produced, $\text{H}_2\text{O} + 2\text{NO}_2 = \text{HNO}_3 + \text{HNO}_2$. That nitrogen peroxide, NO_2 , was not formed in the flame is proved by the fact that this gas decomposes into nitric oxide and oxygen at 620° . Similarly, nitrous oxide, nitrogen tetroxide, nitrogen trioxide and nitrogen pentoxide are excluded. There remains, therefore, only nitric oxide, which is formed in the flame and, on cooling, combines with oxygen of the air to form nitrogen peroxide.

The equilibrium of the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$, according to the law of mass action, is governed, for every temperature, by the function $K = \frac{c_{\text{NO}_2}}{c_{\text{O}_2} c_{\text{N}_2}}$. As the equilibrium of a chemical reaction changes in the sense that the concentration of substances whose formation is endothermic increases with the temperature, and as the formation of nitric oxide is endothermic, K rises with increasing temperature and approaches zero as the temperature falls. If the reaction velocity remained the same for all temperatures, no matter how great the value of K at high temperatures might be, no nitric oxide would be formed, because, at a given high temperature, if a certain concentration were attained, as the temperature was lowered the concentration would lessen with the lowering. The reaction velocity, however, depends chiefly on temperature; in this reaction it is immeasurably small at 1000° , very great at 2000° . This change renders it possible to nearly retain the high temperature concentration by quickly cooling the gases; of course some nitric oxide must be decomposed as the temperature falls, but the more rapid the cooling the less the decomposition.

Hence the ideal nitric oxide formation requires high temperature and rapid cooling. These conditions may be realized in a laboratory by an electrically heated platinum wire in the axis of a cooled tube, but the temperature at which the yield of nitric oxide is enough for a technical process lies far above the fusion point of platinum, and, for technical use, only electric discharges need be considered. These are of two types, arcs and flames; before comparing them we must understand the nature of the flame.

Spottiswoode's observations were carried further by Rayleigh and by Kowalski, who showed that an electric flame cannot be formed directly by a constant tension current, but that high resistance, by induction coils, is needed. Muthmann and Hofer¹ published an extended study of the flame which is carried on by Brode in a part of this monograph. They tried to determine the scientific basis of the technical processes, and were the

¹ Ber. d. chem. Ges., 36, 438 (1903).

first to prove clearly that the nitrogen oxidation is a purely thermal effect. They showed that, in the electric flame, an equilibrium of nitrogen, oxygen and nitric oxide is formed. Their description of the flame is as follows: The nitrogen-oxygen flame resembles in form a gas flame issuing from a slit burner. Three zones can be distinguished; zone 1 is a greenish white band of light, filling an arched space between the electrodes; above this is zone 2, a luminous, greenish blue zone which, with 4 cm. distance between electrodes, is about 5 cm. high; this is surrounded by zone 3, a large outer zone "pale yellowish-brown" in color. The size of the flame increases with the distance between the electrodes. Muthmann thinks that electrical action occurs only in zone 1, the oxidation of nitrogen to nitric oxide in zone 2, and the oxidation of nitric oxide to nitrogen peroxide in zone 3. Brode proves that electrical action is confined to zone 1, by introducing solids into the three zones; a solid may be brought into zone 2 or 3 without altering the strength of the current or its tension, but if a solid is brought into the upper part of zone 1 it flattens the arch, shortening the distance of zone 1 between the electrodes, thus increasing the strength of the current and, if the solid is introduced into the lower part of zone 1, it lengthens the zone and thus decreases the current strength.

Enough has been said of the flame to understand a comparison of the technical value of flame and arc. In the flames the hottest space is comparatively small, and the different temperature zones are approximately equal in area, hence the conditions for cooling are bad. With intermittent sparks or arcs a larger heated area for nitric oxide formation is secured, while the cooling process is rapid, because there are no zones of diminishing temperature as in the flame, and also because, while a flame is a continuous source of heat, broken arcs or sparks give alternate heating and cooling periods.

To sum up: The technical process should employ intermittent arcs or sparks, should work with low current and high resistance, should use a rapid alternating current, should secure temperatures of 2000° and upwards, should provide rapid cooling of the gases, and should have a sparking chamber so arranged that a current of air passes quickly but thoroughly through to the zone of highest heat and out of the chamber. It will be noticed that the need of a low current must mean low total yield of acid, and this is the weak spot in the previous processes. Birkeland, who is professor of physics in the University of Christiania, and Eyde, who is a Norwegian civil engineer, have invented a process¹ which meets these demands

¹ *Electrochem. Indus.*, 2, 399. Various patents.

excepting that for a low current ; the inventors, instead of working with arcs of the lowest possible amperage, make the first technical application of a phenomenon previously known to physicists, the action of the magnetic field on the arc. Both Witt and Brode think this process a technical and financial success ; Witt is, without doubt, an authority on questions of technical chemistry.

The inventors use a powerful current of electricity in the form of great glowing electric discs, which are built up of arcs deflected by powerful magnets as shown in Figs. II. and III.

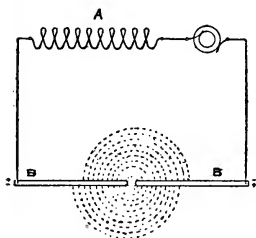


Fig. II.

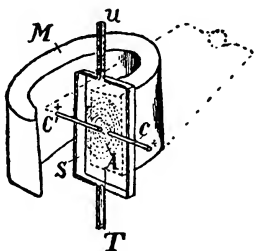


Fig. III.

An induction coil, Fig. II., A is introduced into the circuit and the electrodes BB are placed horizontally. Vertical to the electrodes are powerful electromagnets ; the arc formed between the electrodes is blown away, as it were, by the influence of the magnetic field, and at once a new arc is formed which is blown away ; this process can be repeated 1000 times a second, though in practice only a few hundred arcs per second are used. With alternating current arcs and direct current magnetic field, or *vice versa*, the arcs vibrate between the electrodes as circular discs, as indicated in Fig. II. With 30 kilowatts energy discs of 1 meter diameter can be formed. The electrodes are brought so close together that they would be short-circuited were it not for the magnetic field whose dispersing influence gives sufficient resistance. The hollow electrodes are of copper, cooled internally by water. Fig. III. illustrates the application. M is a magnet ; between its poles is the discharge furnace A, resembling in form a shallow covered box, into which extend the electrodes CC' ; the electric disc is indicated by the circular dotted lines ; air passes rapidly

through the tubes T and *u*, over the disc and out of the furnace. In practice the furnace is built of fire-clay plates, covered externally with copper, and is shown in its latest form in Fig. IV., where A A are electrodes, B B magnets.

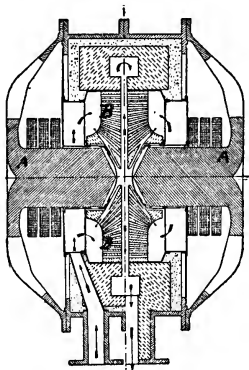


Fig. IV.

This large furnace works with an energy of 500 kilowatts and 5000 volts tension, with alternating current arcs and direct current magnetic field. The electric disc is 2 meters in diameter, and its dazzling, sun-like appearance is photographed in Fig. V.

The yield is about 100 grams of HNO_3 per kilowatt hour, an advance on the 88 grams of the Bradley and Lovejoy process, but this comparison in no sense represents the immense advantage of the Birkeland-Eyde process. The point is that, with the electric disc, the inventors employ 500 kilowatts energy in one furnace, whereas, by other processes, not more than 500 watts could be employed in one furnace. Thus Birkeland and Eyde can make 1000 times as much acid in one furnace in a given time as any of their predecessors. Their new factory at Notodden is equipped with three of the large furnaces described, and the yield is the amount of nitrate corresponding to 1500 kilos of HNO_3 per 10-hour day. The company exploiting the patent has options on the use of Norwegian waterfalls which will yield 350,000 horse power at a very low price, with water carriage to the sea.

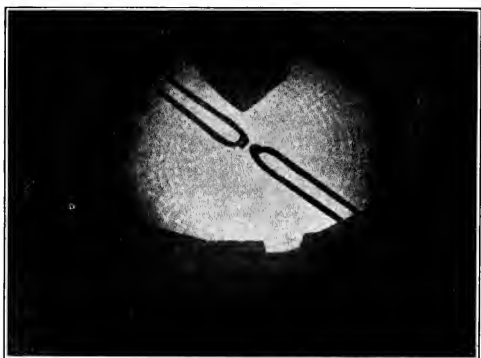


Fig. V.

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The product of the process is a mixture of unchanged air and nitric oxide, containing 2 per cent of the latter, the oxide, of course, combining with the oxygen of the air to form dioxide, which, in turn, with water yields nitric acid and nitric oxide, $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$. This diluted product is unavoidable, as shown by Naville and Guye, but forms the chief objection raised by critics against all previous processes. The following figures will show the reason: The actual cost of the electrical energy required for the oxidation is small. If we say 0.5 pfennig per kilowatt hour (at Notodden it is less) and assume that 10 kilowatt hours energy = 1 kilo HNO_3 ; or, in other words, that the energy required to produce the nitrous gases sufficient to yield 1 kilo of concentrated nitric acid costs 5.2 pfennigs or about 1.2 cents, then, as the German market price of crude nitric acid is 50 pfennigs or 12 cents per kilo, this is 10 times the price of the energy; hence, as Haber pointed out in 1903,¹ the difficulty is less in the production of the nitrous gases than in changing these gases to concentrated nitric acid. This last problem has not yet found its technical solution; doubtless it will be solved, just as the similar problems of the technical treatment of sulphur dioxide to form sulphuric acid and sulphur trioxide have been solved. For the present, the only economical treatment is to market the product in the form of calcium nitrate. In former processes the nitrous gases were conducted directly into milk of lime, forming a mixture of nitrate and nitrite, which, though a good fertilizer, was very hygroscopic and impossible to handle commercially.

The methods by which Birkeland and Eyde have improved and simplified this treatment are interesting: The hot nitrous gases coming from the furnace are cooled by passing under boilers, thus generating steam which is used to concentrate the calcium nitrate solutions. The cooled nitrous gases reach the "oxidation towers," which are lined with acid-proof stone, and merely serve to lessen the movement of the gas current, giving the gas more time for oxidation. The gases now go to the "absorption towers;" these are built of granite and filled with pieces of quartz. Water drips constantly through this tower, absorbing the dioxide; the nitric acid which flows out is returned again and again until it is concentrated to 50 per cent HNO_3 . The gases from the three Notodden furnaces pass through 8 absorption towers, which extract the acid so far that further treatment with water is useless. The gases then pass through two towers filled with milk of lime and one filled with

¹ Z. Elek. Chem., 9, 385.

dry quicklime; all oxidized nitrogen is absorbed; the product is chiefly calcium nitrite, which is treated in closed vessels with some of the 50 per cent nitric acid, and the resulting nitrous gas passed into the "oxidation towers," where it is oxidized quantitatively to nitric acid. All of the nitric acid is neutralized with limestone, the solution is added to that from the nitrite treatment, evaporated and fused; the molten mass is run into iron drums and solidifies on cooling.

This product is not the hygroscopic nitrate $\text{Ca}(\text{NO}_3)_2$, but a basic nitrate which powders readily and, in contact with the soil, *i. e.*, carbon dioxide and moisture, breaks down into normal calcium nitrate and calcium carbonate; that this is good for soils poor in lime, that lime is a better base for fertilizer than the sodium of Chili saltpetre, and that the synthetic nitrate is free from the harmful perchlorate and chlorides of Chili saltpetre, are obvious facts. Indeed, the demand for the synthetic nitrate exceeds the supply.

The Chilean statistician, Vergas,¹ basing calculations on the exportations of Chili saltpetre since 1840, proves that the next 20 years will completely exhaust the South American deposits. No other large deposits are known, nor is their discovery probable.

In the future we must obtain the nitrogen compounds required for agriculture, explosives and all other scientific and technical purposes from the nitrogen of the air.

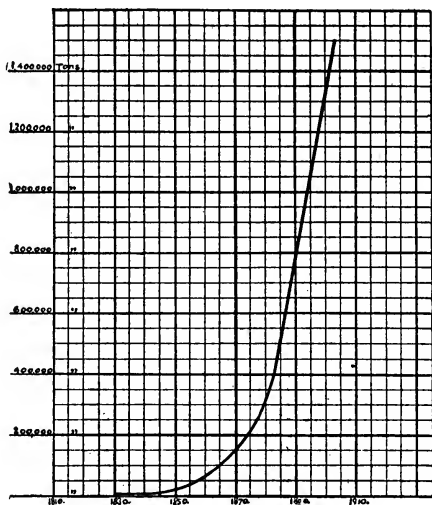
Fig. VI. shows the curve indicating the export of Chili saltpetre from 1830 to 1905. It will be seen that in 1905 1,500,000 tons were exported. Of this $\frac{1}{3}$ was utilized for making nitric acid and other nitrates, the other $\frac{2}{3}$, or 1,200,000 tons, were put on the soil as fertilizer.

Four-fifths of the products from atmospheric nitrogen, then, will be needed for the soil. Thus far there are four methods of combining this nitrogen, one bacterial and three chemical. The bacterial absorption of nitrogen is, at present, confined to leguminous plants, and unless a more active breed of bacteria can be developed, bacterial action, while valuable, cannot replace the use of Chili saltpetre.

The formation and decomposition of nitrides is the second method. This works best with lithium, but barium or calcium might be substituted: $6\text{Li} + \text{N}_2 = 2\text{NLi}_3$ and $2\text{NLi}_3 + 6\text{H}_2\text{O} = 6\text{LiOH} + 2\text{NH}_3$. Now it can be shown that the electric energy required to regenerate this quantity of metallic lithium from the hydroxide, by electrolysis, is about half of that required to oxidize the equivalent quantity of nitrogen to nitrous

¹ Chem. Indus., 1904, p. 29.

gases, while the ammonia generated could be absorbed by water or acid at small expense; yet technical difficulties and the certain loss of some of the valuable metal in the electrolysis



Weltverbrauch an Chilesalpeter 1830-1905.

Fig. VI.

forbid any practical application of this principle, for the present at least.

The third method is Franks' well known process, in which pure nitrogen, not air, is absorbed by heated calcium carbide, forming calcium cyanamide, which is a valuable fertilizer. This process is on trial technically. Whether the calcium cyanamide can compete with the synthetic nitrate is doubtful.

The fourth method is the nitrogen oxidation.

Of one thing we may be certain, by the time the Chili salt-petre beds are exhausted, chemists and engineers will be ready with practical and economical methods of utilizing atmospheric nitrogen to meet the demands of agriculture and industry.

E. RENOUF.

Esterification.

The experiments of E. Fischer and A. Speier,¹ proving that mixtures of organic acids and absolute alcohol could be readily esterified by the use of small quantities, not exceeding 1-5 per cent, of hydrochloric or sulphuric acid, are justly regarded as a most important advance in the preparation of this class of compounds. Later, the present writer² showed that ordinary 90-95 per cent alcohol could be employed with equally good results, provided that the quantity of mineral acid was increased. No improvement has been made in the application of this reaction since that time until the recent publication of a paper by A. Bogojawlensky and J. Narbutt,³ recording the results of an investigation of the action on mixtures of various organic acids and alcohol, of the following dehydrated sulphates: Sodium, ferrous iron, nickel, manganese, copper, cobalt, zinc and potassium pyrosulphate. Sodium sulphate was devoid of action, as was to be expected from the ease with which it parts with its water of crystallization. As a rule, the best results were obtained with potassium pyrosulphate and copper sulphate, with which, therefore, the majority of the experiments were conducted. The former is equally well applicable to aliphatic and aromatic acids, the latter chiefly to the aliphatic acids, but mixtures of copper sulphate (35 grams), with concentrated sulphuric acid (1 gram), gave good results with aromatic acids. In many cases the yields were better than by Fischer's method and the isolation of the ester is usually effected by simply decanting from the salt and fractionating directly. Two other points of considerable interest are brought out in the paper. The one concerns the very marked influence on the yield of ester exercised by traces of sulphur trioxide, such as are present in dehydrated sulphates; for instance, succinic acid (20 grams), alcohol (80 grams) and ferrous sulphate (25 grams), after boiling during 4 hours, gave 85 per cent of the theoretical yield of neutral ester, but on repeating the experiment with anhydrous ferrous sulphate, which had been freed from sulphur trioxide by repeated extraction with alcohol, the yield was only 34 per cent of the theory. An experiment was carried out with malonic acid, alcohol and the zeolite chabasite, which readily absorbs moisture, in order to ascertain if the acceleration in the esterification, which is caused by strong acids and by certain salts, is due simply to the absorption of the water formed by the union

¹ Ber. d. chem. Ges., 28, 3252 (1895).

² THIS JOURNAL, 21, 256 (1899).

³ Ber. d. chem. Ges., 38, 3344 (1905).

of the organic acid and alcohol, or whether these accelerators have some other influence. The result showed that the zeolite had no appreciable effect on the production of ester.

It is to be hoped that the authors will continue their work, because it promises to be of considerable importance for the preparation of esters and may, possibly, help in the elucidation of the mechanism of this puzzling reaction.

Shortly after the publication of the preceding paper J. Wade¹ described a method for the continuous preparation of esters at 100°, in the presence of sulphuric acid. Markownikoff² described a continuous method of esterification 30 years ago, but stated that the reaction does not take place below 130°. Wade finds that the chief factor for success is the rate and extent of the heating; if the flask containing the mixture is placed *on* a water-bath the reaction soon ceases, but if it is *immersed in* the bath, so as to volatilize the water produced by the reaction, the process is truly continuous. It may be interrupted at any time without detriment, and there is no delay in restarting when once the materials have regained the necessary temperature. The presence of sulphuric or some other strong acid is essential, but a large quantity of it is a disadvantage; charring is unusual, so that it is seldom that sulphuric acid cannot be employed. The author states the conditions for the production of ethyl acetate as follows: Three volumes of alcohol are mixed with 2 volumes of acetic acid, and 2 volumes of this mixture are added to 1 volume of sulphuric acid in an Erlenmeyer flask, which is immersed in a water-bath until distillation commences; this may require as much as 30 minutes, but depends on the ester. The mixture of alcohol and acetic acid is then added through a funnel with a fine stem, as in the ordinary preparation of ether. The process is fairly economical, because most of the excess of alcohol is recovered in the purification of the product.

Details of the preparation of other esters are reserved for a subsequent communication, which will be awaited with considerable interest. The method is applicable to all the simple aliphatic and to many of the more complex and aromatic esters, the operation being carried on under reduced pressure when working with the less volatile ones.

J. BISHOP TINGLE.

¹ J. Chem. Soc., 87, 1656 (1905).

² Ber. d. chem. Ges., 6, 1177 (1873).

REVIEWS.

SECOND YEAR CHEMISTRY. A Handbook for Laboratory and Class Work. By EDWARD HART, PH.D., Professor of Chemistry in Lafayette College. Easton, Pa.: The Chemical Publishing Co. 1905. Price, \$1.25.

Professor Hart's preface explains the difference between his book and most laboratory manuals as follows: "In teaching qualitative analysis I have often thought that if the beginner first made some careful quantitative determinations, he would quickly learn the necessity of extreme care and that all his subsequent work would be thereby improved."

In the first 56 pages the author treats, with suitable experiments, of molecules and atoms, properties of gases, gas analysis, dissociation, dissociation in solutions, the chemical balance, volumetric analysis and gravimetric analysis. Seventy-five pages are given to qualitative analysis, and 22 pages, at the close, to different quantitative determinations.

On the whole, the little manual makes a very favorable impression, and we can well believe that Professor Hart has obtained good results with this method. E. R.

ENGINEERING CHEMISTRY. A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists and Engineers. By THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Third edition, with 139 Illustrations. Easton, Pa.: The Chemical Publishing Co. 1905. Price, \$4.50.

In a review of the second edition of this book,¹ Professor Mallet refers to the absence of chapters on lime, lime mortar, stucco and explosives. It is to be regretted that these chapters are also lacking in this third edition. However, the book contains many improved methods of analysis and other important additions, especially the chapters on lubricating oils, cements and asphalt. The volume is well indexed and is provided with abundant references. In its present form this is one of the best practical manuals for engineers and students of engineering. E. R.

THE ELECTROLYTIC DISSOCIATION THEORY, WITH SOME OF ITS APPLICATIONS. An Elementary Treatise for the Use of Students of Chemistry. By HENRY P. TALBOT, PH.D., Professor of Inorganic and Analytical Chemistry, and ARTHUR A. BLANCHARD, PH.D., Instructor in Inorganic Chemistry at the Massachusetts Institute of Technology. New York: The Macmillan Co. London: Macmillan & Co., Limited. pp. 84. Price, \$1.25.

The appearance of this admirable little volume will be wel-

¹ THIS JOURNAL, 25, 517.

comed by all who are interested in the teaching of chemistry from the standpoint of the generalizations reached by physical chemistry. It is indicative of the signs of the times that books of this character are demanded by teachers and students. The general impression is gaining ground, and gaining it rapidly, that the fundamental generalizations which have done so much towards placing chemistry upon a scientific basis, should be taught in the early stages of the study of this subject. They should, of course, be introduced cautiously and in a very elementary form. The chemistry of the atom should not be taught for a year or two and then the student be told that this was all wrong, that atoms do not, in general, react chemically, but that what actually reacts are the ions.

If the student is started in this fashion the question is, how long will it require for him to recover from these first erroneous impressions, or will he ever completely recover? In many cases it is doubtful. If we ask, why continue along the old lines, about the only answer is that the atom is simpler to teach than the ion. This, even if true, would be a sorry reason for teaching what, later, must all be unlearned.

It seems a fair question to ask whether the real reason, in many cases, why the chemistry of the atom is taught, is not to be found in the fact that this is the chemistry which the teacher learned in his earlier days, and it is easier to continue in the old beaten tracks than to become familiar with the newer developments?

The volume under review will contribute its share towards changing this condition of things. The contents are judiciously selected, and the book is clearly written. Chapter I. deals with evidences for the theory of electrolytic dissociation; Chapter II. with the law of mass action and the chemical behavior of electrolytes; Chapter III. with electrolytic solution pressure; Chapter IV. with oxidation and reduction; and Chapter V. with the more common ions and their characteristics. This chapter is especially valuable in connection with the operations of qualitative analysis.

The book is heartily recommended to students, and especially to teachers of elementary chemistry. H. C. J.

AN ELEMENTARY LABORATORY COURSE IN CHEMISTRY. By FRANK B. KENRICK, M.A., PH.D., Lecturer in Chemistry, University of Toronto, and RALPH E. DELURY, M.A., Fellow in Chemistry, University of Toronto. Toronto: Morang & Co. 1905. Price, \$1.00.

In reviewing this volume it must be kept in mind that it is a manual of laboratory work to accompany a course of lectures for beginners in inorganic chemistry, and that the exceptional

features of the book are intended, as we shall see, to meet exceptional conditions.

The preface says: "Owing to the shortness of time in the laboratory, many important principles have been necessarily omitted. The principles especially emphasized, however, are those which, on account of their inherent difficulty or of some traditional error in previous instruction, generally appear to give most trouble to the student."

The experiments—many of them roughly quantitative—are chosen with excellent skill for the purpose in view, which is to devote all the time to illustrating the chief laws and principles of chemical action, thus omitting the systematic laboratory study of the properties of the elements and their compounds, which forms a part of the first year laboratory work in most American colleges. The subjects, which are very clearly treated and accompanied by good, and often ingenious experiments, include solution, crystallization, combustion, combining weights, acids, bases, salts, gravimetric and volumetric analysis, volume relation of gases, reversible reactions, mass law, electrolytic dissociation.

When the time available for laboratory work is very limited, it is, perhaps, better to employ it as is done in this book than to attempt to cover as much ground as is common in the average beginners' laboratory course. Should it be necessary to choose, it is better to understand combustion than to know the properties of all of the oxides of nitrogen. If we regard this book as a protest against the too common method of cramming the beginner with details, while making little attempt to study experimentally the fundamental laws of chemistry, it merits respectful attention.

One peculiarity challenges notice. The authors say in their preface: "All reference to the atomic and molecular theories have been avoided, not because the authors are prejudiced against these excellent hypotheses, but in order to counteract a prejudice in the opposite direction on the part of the students. A large number of students still continue to come to the university with their minds simply stuffed with atoms and molecules, which they take to be the fundamental facts of chemistry."

This experience is not new, probably all college teachers have to combat such fallacies, often brought about by injudicious instruction in the preparatory school; it is true that teachers generally do not apply such drastic discipline as to forbid further indulgence in atoms and molecules, but this may be necessary in Ontario.

Let us examine the authors' plan; instead of atoms they use the idea of combining weights, which they call "reacting weights." Of course it is possible to study most elementary principles and facts of chemistry without reference to atoms and molecules; the question is, does it pay? Does the student get clearer ideas without them? If a lion should hold the path, like ozone for instance, one can pass by on the other side and silently ignore it, but some things cannot be ignored and these are discussed in an appendix; for example, the question arises, why write hydrochloric acid HCl and not H_2Cl_2 or H_3Cl_3 ? here is the explanation:

"It has been discovered that the weights of equal volumes of gaseous chemical substances stand, approximately, in the ratio of simple multiples of their reacting weights when the pressure and temperature are the same. Hence, by choosing these particular multiples of the reacting weights, the numbers obtained will represent, approximately, the weights of equal volumes of the gaseous substances. These are called molecular or formula weights because the chemical formulæ are so chosen as to represent these weights, in addition to the composition."

Is this an improvement on the explanations given commonly? Is the molecular weight less hurtful to the student when christened formula weight?

Some students come to universities overstuffed not only with atoms and molecules but with ions and electrons, and even with reacting weights. Are we, therefore, to throw all these conceptions overboard? However, we must remember that this is only a laboratory manual and that in the lectures the authors probably explain to the student the proper value of those "excellent hypotheses," the atomic and molecular theories.

E. R.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XX Band. Elektrolyse geschmolzener Salze. Erster Teil. Verbindungen und Elemente. von RICHARD LORENZ, PH.D., O. Professor für Elektrochemie und physikalische Chemie, am Eidg. Polytechnikum in Zürich. Mit 9 in dem Text gedruckten Abbildungen. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1905. pp. 217. Price, M. 8.

The author's name on the title-page of this volume leads us to examine it with high expectation, because Lorenz is an authority in the field. We are not disappointed; we find the whole story of the electrolysis of fused salts, from the qualitative preparative point of view, told with great clearness and sense of proportion. Nothing is omitted, all published work is referred to, the lists of patents are complete and yet it is interesting reading; indeed, while we generally look on a mono-

graph like this as a reference work, we find that many of the chapters, notably those on the electrolysis of sodium chloride and sodium hydroxide, of cryolite and of the chlorides of the rare-earth metals, are of absorbing interest.

The author will devote a second volume to the application of Faraday's law, to conductivity and to the subject of electromotive power.

E. R.

DIE ELEKTROCHEMIE DER ORGANISCHEN VERBINDUNGEN. Von DR. WALTHER LÖB. Dritte erweiterte und umgearbeitete Auflage von: Unsere Kenntnisse in der Elektrolyse und Electrosynthese organischer Verbindungen. Halle a. S.: Wilhelm Knapp. 1905. Price, M. 9.

The book is a summary of the work that has been done along the line of the application of the electric current to organic substances. All the principal classes of compounds have been subjected to experiment and the number of reactions that may be effected by the electric current is surprisingly large. The nitro compounds have yielded, perhaps, the most varied and valuable series of products resulting from electrolytic action.

Not only has the direct current been used with great success in producing chemical reactions, but also the alternating current and, in fact, almost all forms of electrical energy. Two factors which must be reckoned with in all operations are the selection of electrodes and the current density. Condensing agents are often used to cause the reaction to stop at a definite stage.

The theoretical side of electrochemical phenomena is treated at some length in the book. The manner in which organic compounds dissociate when treated with the electric current is discussed, and its theoretical bearing clearly stated. The processes which take place around kathode and anode are fully described.

Reactions are classed as primary when the end products have been formed by phenomena directly traceable to the action of the current, and as secondary when the products are the result of a rearrangement or condensation.

The technical value of the electric current in the manufacture of organic compounds is shown to be very great and, since this is only a new field, it is difficult to predict to what extent its application will be carried.

Constant reference is made to the investigations of Löb, Elbs, Walker, Haber, Müller and many others, who are active in the development of this new chapter of organic chemistry.

The book may be recommended to all who are interested in the extension of this important field of research. C. W. G.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, C. A. BISCHOFF, ALFRED COHN, M. DELBRÜCK, J. M. EDER, TH. FISCHER, P. FRIEDLAENDER, C. HAEUSSERMANN, A. HERZFELD, W. KÜSTER, J. LEWKOWITSCH, A. MORGEN, F. QUINCKE, A. WERNER. Herausgegeben von RICHARD MEYER. XIV. Jahrgang, 1904. Braunschweig: Vieweg und Sohn. 1905. Price, M. 14.

The Jahrbuch for 1904 appears after a considerable delay, which the publishers promise to avoid in the future, as they have in the past.

It is a complete review of the progress of the year, arranged so that each piece of work may be considered in relation to other work on similar topics.

The work, as a whole, is well done, as we should expect from the list of co-workers. There are some curious omissions. Several important physical chemical articles, published in this JOURNAL, are omitted and, by a singular coincidence, important work by the same authors, published in the *Zeitschrift für Physikalische Chemie* is also either omitted or barely mentioned, although the other articles in the *Zeitschrift* are reviewed.

E. R.

THE POLARISCOPE IN THE CHEMICAL LABORATORY. An Introduction to Polarimetry and Related Methods. By GEORGE WILLIAM ROLFE, A.M., Instructor in Sugar Analysis in the Massachusetts Institute of Technology. New York and London: The Macmillan Company. 1905. pp. 320.

The subject of polarimetry has, for some time, been of practical importance on account of its use for the commercial testing of sugars. It has recently acquired a scientific significance in connection with the dynamics of the reaction of the inversion of cane sugar. We are frequently in need of information in reference to the use of the various polariscopes, and the significance of the results obtained. The present volume supplies just this information.

The several sections deal principally with the polariscope, the saccharimeter, polarization of cane sugar, commercial methods, determination of sucrose in the presence of other optically active substances, sugar-house and refinery methods, chemical methods of determining sugars, starch and starch products, applications of the polariscope in scientific research, application to chemical analysis.

It will be seen from the above that this review refers to a book which is of both scientific and technical value. It is to be hoped that it will meet with the wide reception that it deserves.

H. C. J.

EXERCISES IN QUANTITATIVE CHEMISTRY. By HARMON NORTHOP MORSE, Professor of Analytical Chemistry in the Johns Hopkins University. Boston, New York, Chicago, London: Ginn & Co. 1905. pp. xx + 556. Price, \$2.00.

Those shelves of our chemical libraries which are devoted to books on quantitative analysis have, if we have been sympathetic purchasers, filled somewhat over-rapidly of late. Many of the contributions to this branch of chemical literature have been the product of careful thought and a painstaking selection of reliable methods, but they have, almost without exception, followed a conventional treatment of the subject. It is, therefore, a real, as it is an unusual pleasure to receive a volume which presents a course of instruction in quantitative chemistry with distinctive features, and one which is the product of the long experience of a successful teacher.

Professor Morse points out that, with the increasing demands made upon the time of the student of chemical science for instruction in other branches of chemistry, the selection of a suitable general course of instruction in quantitative practice has become increasingly perplexing. He has, therefore, formulated his course in such a way as to give familiarity with the greatest practicable variety of methods and operations, and has included not alone methods of chemical analysis, but also those involving accurate determinations of specific gravity, and determinations of molecular weights. An incidental, but striking and valuable feature of the course, is the thoroughness of the practice which it affords in the determination of the limitations and the accuracy of the instruments employed, a point upon which much stress is laid. The course is, then, one in quantitative chemistry, not analytical chemistry.

The first four chapters deal successively with the balance, the barometer and thermometer, the calibration of eudiometers and the measurement of gases, and the calibration and graduation of apparatus for the measurement of liquids. The first chapter is noticeable for its thorough discussion of methods of testing balances and weights.

Chapter V. deals with standard solutions, Chapter VI. with the determination of specific gravity, Chapter VII. with molecular weights, and Chapter VIII. with the purification of substances, including the general operations of filtration, washing of precipitates, and the like. Chapters IX. to XXII. (pp. 209-516) include quantitative procedures of the most varied character, and the combination of volumetric with gravimetric methods, as well as the application of one or both to organic compounds is unusual and worthy of attention. There are among the exercises examples of the processes involved in gas

analysis, food analysis, and electrolysis, with a clear and concise statement regarding electrical units and the apparatus employed in this class of work. In the last two chapters certain new and useful electrical heating appliances are described, together with an electrical method for the combustion of organic compounds.

The procedures are given in considerable detail and the book contains a great deal of valuable information which cannot be indicated in a brief summary, it is all presented in easily readable form. The particular analytical procedures which the author has selected will, doubtless, sometimes excite comment. It would, for example, seem natural to give preference to the Drown method for the determination of silicon in irons or steels, especially since the dehydration of silicic acid by sulphuric acid is not otherwise emphasized, or to replace copper ammonium chloride by copper potassium chloride in the determination of carbon in irons, in view of the acknowledged sources of error sometimes involved in the use of the former reagent. The omission of a procedure for the separation of iron from manganese is also noticeable, particularly the omission of a process so distinctive in its character as the basic acetate method. The use of the atomic weights based on hydrogen as unity, the retaining of the older definitions for the molecular changes of boiling or freezing point, and an apparent preference, in many instances, for the methods given in the manual of Fresenius may possibly raise a question in the mind of the reader whether or not the author is just a bit too much inclined to adhere to older methods, or points of view, rather than to incorporate more recent work. But these, so far as the main purpose of the book is concerned, are minor matters and should not deter any teacher or student from according it the careful examination which it undoubtedly deserves.

The book is thoroughly indexed and exceptionally well printed and bound.

H. P. TALBOT.

BEET SUGAR MANUFACTURE AND REFINING. Vol. I.: Extraction and Epuration. By LEWIS S. WARE. New York: John Wiley & Sons. London: Chapman & Hall. 1905. Price, \$4.00.

This volume of 537 pages of text, yet treating of only two of the basic processes of beet sugar manufacture, is by far the most comprehensive work on beet sugar technology which has appeared in the English language.

The author states that he limits his work strictly to a compilation of the data and discussions of European literature as best giving expression to the practice of the world's leading experts. He refrains from consideration of American methods on the ground that he would be obliged to criticize "some very

glaring blunders." No doubt many blunders have been made in America, yet it would seem that processes of beet sugar manufacture are not yet so far developed as to be standard even in Europe. The author says, in his preface: "In fact, throughout the entire realm of sugar manufacturing, there is a vast budget of contradictions." Hence a discussion of methods extant in successful American factories might have been of profit, particularly as it is a matter of common knowledge that foreign experts, as a rule, have not been satisfactory in American practice.

The 22 pages of the introductory chapter discuss the economics of the industry from a practical standpoint. The suggestions for utilizing beet sugar factories during the "dead" season are most interesting. Incidentally, the reviewer dissents from the author's carbonation scheme for manufacturing *milk* sugar as quite impracticable, although it might be that the plant could be utilized in other ways for this purpose.

Considering the book as a whole, the material is judiciously chosen, and evidently by an expert of some experience. The references to authorities are very complete and the illustrations are many and excellent. In the opinion of the reviewer, however, the book is somewhat marred by the style of the English, which occasionally follows the German and French constructions so literally as to make it evident which was the language of the original, and, in fact, almost to permit of reproduction of the foreign text. Naturally, in such cases, the English is clumsy and lacks compactness, particularly in excerpts from the German. Such expressions as "conservation of beets," "surveillance of washer" (machine), "fixation of knives" (in slicing machines) possibly may have a certain vogue in beet sugar factories here, but certainly are not those of the best usage; and "arrival and departure of the juice into the diffusers," "forged iron piping" and "axis of rotation" (for shafting) are some of the examples, among others, which might be cited as especially unhappy rendering into technical English. As a rule, however, the descriptive matter is clear enough to be readily understood by the engineer and manufacturer, who will be greatly assisted by the illustrations with which the book abounds.

The discussions of rationale of process are a valuable feature, and cannot fail to be instructive.

The book would have been improved if dimensions of machinery and other factory measurements had been expressed in the standards in common use in English-speaking countries.

The presswork, as a whole, is of high quality.

GEO. W. ROLFE.

AMERICAN CHEMICAL JOURNAL

CAMPHORIC ACID: SOME DERIVATIVES OF AMINOLAURONIC ACID.

[FIFTEENTH PAPER.]

BY WILLIAM A. NOYES AND RENÉ DEM. TAVEAU.

*see errata
p 570.*

When the nitroso derivative of the anhydride of amino-lauronic acid is boiled with an aqueous 10 per cent solution of sodium hydroxide, in the proportion of 1 molecule of the nitroso body to 1.5 molecules of sodium hydroxide, there result, besides the products already described, compounds that have not been obtained under the conditions of decomposition hitherto studied.

The several products of the decomposition and their percentage weight of the nitroso body are, approximately, as follows:

Hydrocarbon, C_8H_{14}	27.8 per cent
Substances volatile with water vapor:	
Isocampholactone, C_8H_{14} $\begin{array}{c} \diagup \text{CO} \\ \\ \text{O} \end{array}$	21.4 "
An unsaturated acid, $C_8H_{13}CO_2H$	6.6 "

Liquid acids, mainly γ -lauronic acid(?)	1.4 per cent
Substances not volatile with water vapor :	
Impure hydroxylauronic acid,	
$\text{C}_8\text{H}_{14} \begin{cases} \text{CO}_2\text{H} \\ \text{OH} \end{cases}$	1.7 "
A new lactone, $\text{C}_8\text{H}_{14} \begin{cases} \text{CO} \\ \\ \text{O} \end{cases}$	4.0 "

Briefly stated, the method of obtaining and separating these products was as follows: The nitroso compound, once crystallized from strong alcohol, was introduced into a roomy flask; the required amount of aqueous 10 per cent sodium hydroxide solution added, the flask connected with a return condenser and the contents gently boiled over a free flame until the supernatant layer of hydrocarbon was practically colorless, which required about 2 hours.

The method of separating the products of the reaction was essentially the one already described by us¹; the only modifications necessary were that the hydroxy acid was shaken with strong potassium carbonate solution to separate it from the new lactone, and that the γ -lauronic acid portion was subjected to a fractional distillation, under diminished pressure, to separate this acid from the crystalline unsaturated acid accompanying it.

Isocampholactone.—This was purified by distilling it under diminished pressure. It boils at $123^\circ.4$ (28 mm.) or at $125^\circ.6$ (30 mm.). It melts at 32° – 33° . An attempt was made to prepare the ethyl ester of the hydroxy acid corresponding to the lactone. It was hoped that by the oxidation of the ester we could obtain the ester of camphononic acid, and thus secure some evidence as to the structure of the lactone. A considerable quantity of the silver salt of the hydroxy acid was prepared as previously described.² An analysis of the salt gave 38.62 per cent of silver. Calculated, 38.68 per cent. This salt was allowed to stand for 2 weeks with a large excess of methyl

¹ THIS JOURNAL, 32, 288.

² *Ibid.*, 32, 290.

iodide and some absolute ether, care being taken to exclude the light. The silver iodide was separated by filtration, and the excess of methyl iodide and ether by distillation under diminished pressure. The product of the reaction, a dark brown oil, was diluted with ether and shaken with a solution of sodium thiosulphate, to remove free iodine which was present. The ether solution was washed with water, dried with calcium chloride and the ether removed under diminished pressure. The product, which was now nearly colorless, was analyzed.

I. 0.1561 gram substance gave 0.3931 gram CO_2 and 0.1273 gram H_2O .

II. 0.1493 gram substance gave 0.3756 gram CO_2 and 0.1220 gram H_2O .

	Calculated for $\text{C}_8\text{H}_{14}\begin{matrix} \text{CO} \\ \\ \text{O} \end{matrix}$		Found.	
	$\text{C}_8\text{H}_{14}(\text{OH})\text{CO}_2\text{CH}_3$		I.	II.
C	70.06	64.45	68.67	68.60
H	9.17	9.76	9.14	9.15

It is evident from the analyses that the product consisted chiefly of unchanged lactone. Thinking that the ester might have been formed at first, and then saponified by the long standing, the mixture was again treated with potassium hydroxide and the silver salt prepared as before. This was boiled for 2 hours with methyl iodide and ether and the product separated as before. It gave now : C, 68.91 ; H, 9.30.

Methyl Ether of the Hydroxy Acid Corresponding to Isocampholactone, $\text{C}_8\text{H}_{14}(\text{OCH}_3)\text{CO}_2\text{H}$.—To separate the mixture contained in the above product into its constituents, it was subjected to fractional distillation. The isocampholactone passed over first, leaving a viscous oil, which boiled at about 150° – 153° (19 mm.) and solidified on cooling. The compound separates from its solution in isocampholactone in large, compact, beautiful crystals. After solution in sodium carbonate, removal of a small amount of isocampholactone by extraction with ether and reprecipitation with hydrochloric acid, it is deposited in microscopic needles, which melt at 84° .

I. 0.1870 gram substance gave 0.4443 gram CO_2 and 0.1616 gram H_2O .

II. 0.1609 gram substance gave 0.3834 gram CO_2 and 0.1373 gram H_2O .

	Calculated for $\text{C}_8\text{H}_{14}(\text{OCH}_3)\text{CO}_2\text{H}$.	I.	Found. II.
C	64.45	64.80	64.70
H	9.76	9.69	9.57

0.0889 gram of the substance required for its neutralization 4.76 cc. 0.1 N barium hydroxide. Theory requires 4.78 cc. ; 0.1346 gram of the resulting barium salt gave 0.0622 gram BaSO_4 , corresponding to 27.20 per cent Ba. Calculated for $[\text{C}_8\text{H}_{14}(\text{OCH}_3)\text{CO}_2]_2\text{Ba}$, 27.07 per cent.

On warming with hydriodic acid in the manner used by Zeisel¹ for the determination of methoxy groups, methyl iodide was eliminated.

While the formation of an ether of the formula given, under the conditions of our experiments, appears very remarkable, the conduct of the compound and the results of the analyses seem to leave no doubt with regard to the nature of the substance.

Substances Volatile with Water Vapor, Other than Isocampholactone.—These were separated by fractional distillation under reduced pressure, using a Claisen bulb with a delivery tube consisting of two 50 cc. bulbs connected together and to the flask by tubing 1.5 cm. in diameter ; tubing of 0.5 cm. diameter connected the bulb farthest from the flask with the rubber tubing to the pump. Such a side tube was found advantageous, owing to the tendency of the new crystalline, unsaturated acid to sublime into and choke the ordinary delivery tube.

After this acid had been distilled, in all, about 10 times, its boiling point was $130^\circ\text{--}133^\circ$ (21 mm.).

The liquid fraction boiled between $137^\circ\text{--}150^\circ$ (22 mm.) and probably consisted largely of γ -lauronic acid. Its silver salt gave 41.34 per cent Ag. Calculated, 41.33 per cent.

There remained in the distilling bulb, after the liquid por-

¹ Monats. Chem., 6, 789; 7, 406.

tion had passed over, a viscous oil that crystallizes, on long standing, and in a form apparently different from that of the unsaturated acid. The crystals were dissolved in potassium carbonate solution, this solution extracted with ether, then acidified and the acid recovered. It gave a melting point of 90° – $90^{\circ}.5$. The amount of this acid was too small for further examination.

The Crystalline Unsaturated Acid, $C_8H_{13}CO_2H$.—This dissolves slowly in cold, concentrated potassium carbonate solution, reduces a cold solution of potassium permanganate instantly and is too readily soluble in the ordinary organic solvents to be recrystallized from them. One-tenth of a gram of the acid neutralized 6.18 cc. of 0.1 N alcoholic potassium hydroxide solution. Calculated, 6.49 cc.

I. 0.1658 gram substance gave 0.4302 gram CO_2 and 0.1347 gram H_2O .

II. 0.2232 gram substance gave 0.5762 gram CO_2 and 0.1818 gram H_2O .

	Calculated for $C_8H_{13}CO_2H$.	I.	Found. II.
C	70.07	70.75	70.40
H	9.17	9.10	9.13

In order to further purify the substance, it was dissolved in very dilute, aqueous potassium hydroxide, and precipitated with dilute sulphuric acid as a snow-white, caseous mass. It was precipitated in this manner 6 times, the first alkaline solution being extracted with ether, and the dissolved ether removed under diminished pressure, before precipitating. It was then twice dissolved in potassium carbonate solution and precipitated as before, the first potassium carbonate solution being extracted with ether to remove any lactones which might be present.

As stated above, the acid boils, or rather sublimes, at 130° – 133° (21 mm.). The acid, separated from its calcium salt, melts at 152° – 154° . A solution of the acid in a solution of sodium carbonate decolorizes a solution of potassium permanganate instantly.

About 10 years ago Walker and Henderson¹ prepared an acid, which melted at 153°, from the mixtures of esters obtained by the electrolysis of potassium alloethylcamphorate. The acid was obtained from that part of the ester which was most difficult to saponify and which had been boiled for a long time with alcoholic potassium hydroxide. It seems altogether probable that the two acids are identical. It is possible that in both cases the acid was formed by the action of the alkali on γ -lauronic ("allocampholytic") acid.

Silver Salt, $C_8H_{13}CO_2Ag$.—This was obtained by precipitation from a solution of the sodium salt. The analysis gave 41.48 and 41.35 per cent Ag. Calculated, 41.33 per cent.

Calcium Salt, $(C_8H_{13}CO_2)_2Ca \cdot H_2O$.—This salt separates in large, well formed crystals. It is more soluble in cold than in hot water. The crystals are efflorescent.

I. 0.1924 gram salt lost 0.0088 gram H_2O at 102° and gave 0.0719 gram $CaSO_4$.

II. 0.1774 gram salt lost 0.0080 gram H_2O at 102° and gave 0.0664 gram $CaSO_4$.

III. 0.3430 gram salt lost 0.0170 gram H_2O at 102°.

	Calculated for $(C_8H_{13}CO_2)_2Ca \cdot H_2O$.	I.	Found. II.	III.
H_2O	4.94	4.57	4.51	4.95
Ca	11.01	11.01	11.02	. .

Substances not Volatile with Water Vapor.—The mixture of these products was fractionated under diminished pressure, in order to obtain, especially, the hydroxylauronic acid, if such were present. The boiling point of this acid is given at 180°–185° (25 mm.).² The fraction obtained under these conditions was extremely small, amounting to less than 1.5 grams, and was impure, as is shown by the following analyses of the product, the impurity, undoubtedly, being the crystalline body which constitutes, by far the larger part of the mixture.


I. 0.1140 gram substance gave 0.2706 gram CO_2 and 0.0941 gram H_2O .

¹ J. Chem. Soc., 37, 343. The melting point is given in that paper as 158°, but Prof. Walker writes me that this is a misprint. W. A. N.

² THIS JOURNAL, 32, 289.

II. 0.1229 gram substance gave 0.2898 gram CO_2 and 0.0998 gram H_2O .

	Calculated for $\text{C}_8\text{H}_{14}(\text{OH})\text{CO}_2\text{H}$.	I.	Found.	II.
C	62.73	64.73		64.31
H	9.38	9.20		9.09

The New Lactone, C_8H_{14} .—The body is deposited from


its solution in ether and by sublimation, in beautiful crystals. Like the crystalline, unsaturated acid, it is too soluble in the usual organic solvents to be recrystallized from them. It does not reduce a neutral solution of potassium permanganate. Fractional distillation, under reduced pressure, was found to be an unsatisfactory method of purification; however, several fractionations of the substance were made, using the Claisen bulb already described. The exact boiling point of the substance was not found, owing to its tendency to sublime. After distilling several times it was observed that at 126° (27 mm.), practically all of the substance had passed over. The pure lactone melts at 164° – 165° .

The substance does not dissolve in strong potassium carbonate solution, and shaking with such a solution affords the best method of separation from accompanying acid substances. The following figures were obtained for carbon and hydrogen, they agree best with the formula $\text{C}_9\text{H}_{14}\text{O}_2$.

I. 0.2848 gram substance gave 0.7280 gram CO_2 and 0.2290 gram H_2O .

II. 0.1416 gram substance gave 0.3620 gram CO_2 and 0.1122 gram H_2O .

III. 0.2208 gram substance gave 0.5694 gram CO_2 and 0.1791 gram H_2O .

	Calculated for C_8H_{14}  .	I.	Found.	II.	III.
C	70.07	69.71	69.72		70.33
H	9.17	9.01	8.85		9.09

The lactone is dextrorotatory; 2.0289 grams, dissolved in

absolute alcohol and diluted to a volume of 20 cc., gave, at 22°.4, in a 2 decimeter tube, a rotation of 2°.82 to the right, from which $[\alpha]_D = +13°.87$.

Hydroxy Acid Corresponding to the Lactone, $C_8H_{14}(OH)CO_2H$.—From a solution of the lactone in barium hydroxide, acids precipitate the corresponding hydroxy acid. This melts at 189°.5, with decomposition but no discoloration.

0.1932 gram substance gave 0.4459 gram CO_2 and 0.1576 gram H_2O .

	Calculated for $C_8H_{14}(OH)CO_2H$.	Found.
C	62.73	62.94
H	9.38	9.14

Silver nitrate gives no precipitate in a solution of the potassium salt of the hydroxy acid.

The *barium salt*, $[C_8H_{14}(OH)CO_2]_2Ba \cdot 4H_2O$, crystallizes well.

I. 0.2260 gram salt lost 0.0284 gram H_2O at 102° and gave 0.0962 gram $BaSO_4$.

II. 0.2105 gram salt lost 0.0262 gram H_2O at 102° and gave 0.0895 gram $BaSO_4$.

III. 0.3821 gram salt lost 0.0480 gram H_2O at 102°.

	Calculated for $[C_8H_{14}(OH)CO_2]_2Ba \cdot 4H_2O$.	I.	Found. II.	III.
H_2O	13.06	12.56	12.44	12.55
Ba	24.90	25.05	25.02	. .

PHARMACOLOGICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1906.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

VIII. REACTIONS WITH α,β -UNSATURATED NITRILES.

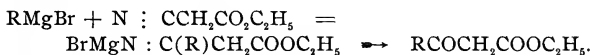
BY E. P. KOHLER.

In an earlier paper¹ it was shown that the reaction between α -cyancinnamic esters and Grignard's reagent does not involve

¹ THIS JOURNAL, 33, 333.

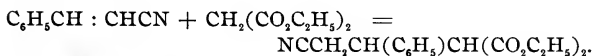
the cyanogen group. This result led to the conclusion that the system, $C:CC:O$, combines with organic magnesium compounds more readily than the system, $C:CC:N$, and this conclusion was supported by some preliminary experiments made with α,β -unsaturated nitriles. In continuation of this work, I began a study of the reaction with esters of α -cyanocinnamylideneacrylic acid, but the results obtained were so complex that it seemed advisable to make a more careful investigation of the reaction with unsaturated nitriles.

It seems probable that the cyanogen group combines with Grignard's reagent more readily than carbonyl, because Blaise found¹ that it is possible to regulate the reaction with ethyl cyanacetate in such a way that only the cyanogen is attacked :



To what extent the properties of the group are modified by the presence of the ethylene linkage is not clear, because very few experiments with unsaturated nitriles have been described ; but the difficulties experienced in hydrolyzing these substances,² and in the efforts made to reduce them to the corresponding amines,³ indicate that the cyanogen in unsaturated nitriles is less reactive than that in saturated compounds.

It is certain that the presence of cyanogen in the α -position greatly increases the apparent reactivity of the ethylene linkage. This is shown by the ease with which unsaturated nitriles are reduced to saturated compounds and, especially, by the fact that these nitriles, like the corresponding unsaturated ketones and esters, readily combine with substances that contain mobile hydrogen. Vorländer found,⁴ for example, that in the presence of sodium ethylate cinnamionitrile adds ethyl malonate, according to the equation :



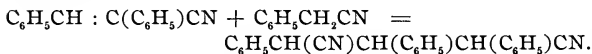
¹ Compt. rend., **139**, 674.

² Ann. Chem. (Liebig), **250**, 157.

³ Ber. d. chem. Ges., **23**, 2859.

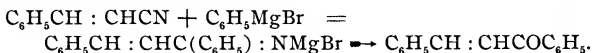
⁴ Ann. Chem. (Liebig), **320**, 98.

Similarly, Henze¹ obtained the nitrile of symmetrical tri-phenylglutaric acid by adding benzyl cyanide to α -phenylcinnamionitrile :



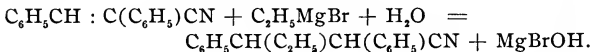
In all of these cases, however, the primary reaction may consist in 1,4-addition to the conjugated system $\text{C} : \text{CC} : \text{N}$, and it was hoped that a study of the reaction between unsaturated nitriles and Grignard's reagent would bring some light on this question.

The experiments described in the present paper were made with cinnamionitrile, α -phenylcinnamionitrile, and β -phenylcinnamionitrile. With the first and last of these, only products similar to those obtained from saturated nitriles could be isolated. Cinnamionitrile and phenylmagnesium bromide, for example, gave benzalacetophenone :



The results obtained with these substances are, however, not conclusive because, as has been found² with nearly all unsaturated compounds having hydrogen in the α -position, the reactions are far from complete and the yields poor.

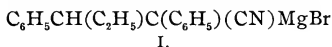
The experiments with α -phenylcinnamionitrile are much more satisfactory because the reactions are, for the most part, quantitative and it is, therefore, possible to account for all of the material that is used. With ethylmagnesium bromide 98 per cent of the final product consists of stereoisomeric nitriles, formed according to the equation :



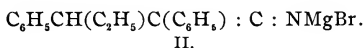
It is evident, from this result, that the reagent combines either with the unsaturated carbon atoms or with carbon and nitrogen in the 1,4-positions. The two possible formulas of the magnesium derivatives are, therefore,

¹ Ber. d. chem. Ges., **31**, 3059.

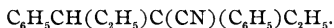
² THIS JOURNAL, **34**, 568.



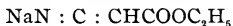
and



In view of the fact that Grignard's reagent does not combine with unsaturated hydrocarbons,¹ and by analogy with the results obtained with unsaturated esters and ketones, the second formula seems, *a priori*, the more probable one. It was found, however, that the magnesium derivatives obtained from nitriles differ markedly from those obtained from esters and ketones. The latter do not react with simple halogen alkyls, and they give O-alkyl derivatives with the unusually reactive diphenylbrommethane. The former react with ethyl iodide in the cold and the products are C-alkyl derivatives. The magnesium derivative from ethylmagnesium bromide, for example, gives



This reaction is exactly like the one that is used for introducing alkyl into substances like cyanacetic ester, malonitrile and benzyl cyanide, by means of metallic derivatives. For these derivatives most writers use a formula analogous to I., but this is done, probably, simply as a matter of convenience, because there is no evidence, that at present can be regarded as valid, in favor of such a formula. Nef² has proposed a formula analogous to II. To account for the reactions of ethylsodium cyanacetate, for example, he uses



and he has succeeded in finding considerable evidence in favor of this arrangement. While this is, in itself, not conclusive, it is supported by all the recent work on tautomerism.

It will be shown, in the experimental part, that most of the reactions of the magnesium derivative can be interpreted on the basis of either formula ; but Formula I. seems improbable

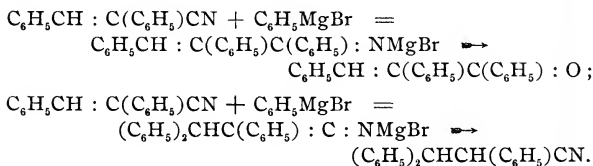
¹ THIS JOURNAL, 31, 642.

² *Ibid.*, 18, 723. Ann. Chem. (Liebig), 287, 265.

on more general grounds. This arrangement represents a complex Grignard derivative containing a tertiary alkyl group, and it is highly improbable that such a substance would be formed by addition to unsaturated carbon atoms when the unsaturated compound contains the much more reactive cyanogen group. Moreover, substances of this type cannot be made by treating a tertiary alkyl haloid with magnesium in the usual way. This was established in the present case by treating the corresponding bromine compound with magnesium. No reaction took place until the unusually reactive magnesium of Baeyer¹ was used, and then the product was a mixture of reduction products that did not contain a trace of reactive magnesium.

The magnesium derivative in question does not behave like a Grignard reagent. It was boiled with acetaldehyde, acetone, ethyl acetate, benzaldehyde and benzophenone, and while the aromatic compounds gave brilliantly colored precipitates, treatment with ice-water in each case resulted in the liberation of unchanged aldehyde, ketone, or ester. These results are not conclusive, because it is known that complex magnesium derivatives do not always react like the simpler substances,² but taking all available facts into consideration, I regard Formula II. as the more probable and, therefore, assume that with ethylmagnesium bromide the reaction consists in 1,4-addition.

With phenylmagnesium bromide the same nitrile gives two products—an unsaturated ketone and a saturated nitrile :



This result is evidently not in harmony with Thiele's theory of partial valences.

¹ Ber. d. chem. Ges., 38, 2759.

² *Ibid.*, 36, 4272.

EXPERIMENTAL PART.

I. α -Phenylcinnamonitrile and Ethylmagnesium Bromide.

Preliminary experiments showed that the action between the nitrile and alkylmagnesium compounds is not influenced by the conditions under which they are allowed to react, and that the nature of the product is not dependent upon the relative amounts of the reagents. In these experiments both ethereal solutions of ethylmagnesium bromide, made in the ordinary way, and ligroin solutions of ethylmagnesium iodide made according to Tschelinzeff were used. In some experiments the nitrile was added to an excess of the magnesium compound, while in others the magnesium compound was siphoned into an excess of nitrile, and in each case one reaction was carried out at the boiling point of the solvent while another was allowed to proceed slowly, at the temperature of a freezing mixture. The primary product is always a dark red substance that is soluble in ether, but insoluble in ligroin, from which it separates as a paste. On treatment with water it gives ethane, unchanged nitrile and magnesium salts. It is, therefore, a double compound containing the nitrile in place of ether.

When the nitrile is added to boiling solutions this red product disappears almost as fast as it is formed, until the solution contains an excess of nitrile, when it becomes permanent. In the cold the disappearance of the color and the occurrence of the reaction take place very slowly, but the amount of nitrile required to produce a permanent color is the same as in boiling solutions. The product, obtained by treatment with water at this stage, contains no unchanged nitrile. If more nitrile is added, before treatment with water, the color becomes deeper and finally blood-red crystals separate from the solution, but when these are decomposed with water the excess of nitrile is recovered unchanged.

In all subsequent experiments the procedure was as follows: Solid nitrile was added, in small portions, to a boiling solution of ethylmagnesium bromide, until a faint but persistent color appeared in the liquid. The resulting solution, which for brevity will be referred to as the magnesium derivative, was

then treated with the various reagents, as described in the following account :

α,β -Diphenylvaleronitrile, $\text{C}_6\text{H}_5\text{CH}(\text{C}_2\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CN}$. — The magnesium derivative was poured on cracked ice, the basic salts dissolved with hydrochloric acid and the ethereal layer washed and evaporated in a draught. It first deposited a hard, granular solid and then a considerable quantity of colorless oil. The oil was drawn off with a pump, the solid washed with cold alcohol and repeatedly recrystallized from boiling alcohol. It was thus obtained in small, lustrous crystals, readily soluble in acetone and boiling alcohol, moderately in cold alcohol and ether. The melting point is 115° .

The oil that accumulated in the mother liquors from this solid was dissolved in ether, the solution dried with sodium sulphate and fractioned under diminished pressure. It was thus separated into two substances: The solid previously described, melting at 115° and boiling at 235° – 240° (20 mm.) and a colorless oil, boiling at 210° – 212° (20 mm.), which remained liquid in a freezing mixture. Both of these substances were indifferent to potassium permanganate in acetone solution—therefore saturated—and a qualitative test showed that both contain nitrogen. The analyses prove that they are isomeric :

I. 0.1560 gram *solid* gave 0.4972 gram CO_2 and 0.1018 gram H_2O .

II. 0.1715 gram *oil* gave 0.5470 gram CO_2 and 0.1158 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{17}\text{N}$.	I.	Found. II.
C	86.81	86.91	86.93
H	7.23	7.25	7.45

As *α,β -diphenylvaleronitrile* contains 2 asymmetric carbon atoms it seemed likely that these two substances represented the two possible racemic modifications. This conjecture was verified by hydrolysis. It was not possible to get more than a trace of acid by boiling either of the substances with alcoholic potassium hydroxide, but complete hydrolysis was obtained by heating them to 180° with concentrated hydrochloric acid, for

4 hours. The result was the same with each substance—a mixture of isomeric acids differing but slightly in solubility in common solvents. The mixture was partially separated by several crystallizations, but sharp melting points were obtained only after many recrystallizations from ligroin.

α,β-Diphenylvaleric Acids, $C_6H_5CH(C_6H_5)CH(C_6H_5)CO_2H$.—The high-melting acid separates from ligroin in very small, lustrous plates, melting at 178° . When free from the lower-melting isomer it is only moderately soluble in ether and very sparingly in ligroin. Analysis:

0.1235 gram substance gave 0.3657 gram CO_2 and 0.0780 gram H_2O .

	Calculated for $C_{17}H_{18}O_2$.	Found.
C	80.30	80.50
H	7.00	7.02

The low-melting acid is also sparingly soluble in ligroin, but it separates from solution much more slowly than its isomer. It is easily recognized in a mixture of the two because it is always deposited in clusters. It is readily soluble in alcohol and ether and it melts at 152° – 153° . Analysis:

0.1380 gram substance gave 0.4063 gram CO_2 and 0.0866 gram H_2O .

	Calculated for $C_{17}H_{18}O_2$.	Found.
C	80.30	80.29
H	7.00	7.02

As each of the nitriles, on hydrolysis, gave a mixture of these two acids, it seemed probable that the acids could be mutually transformed by heating with concentrated hydrochloric acid. This was found to be the case. After heating at 180° , for 24 hours, each gave a mixture of the two acids.

α-Ethyl-α,β-diphenylvaleronitrile, $C_6H_5(C_2H_5)CHC(C_2H_5)(C_6H_5)CN$.—The magnesium derivative was treated with a little more than the calculated quantity of ethyl iodide and the mixture boiled for several hours. The resulting clear solution was poured into ice-water and the

product isolated in the usual way. The reaction is a remarkably clean one and 98 per cent of the unsaturated nitrile used in the preparation of the magnesium derivative is contained in the single substance isolated. This was easily purified by crystallization from alcohol or ligroin. It crystallizes in large tabular plates, melting at 105° , readily soluble in acetone, alcohol, ether and chloroform; moderately in ligroin. Analysis:

I. 0.1464 gram substance gave 0.4643 gram CO_2 and 0.1082 gram H_2O .

II. 0.4011 gram substance gave 19.5 cc. N at 21° and 755 mm.

	Calculated for $\text{C}_{19}\text{H}_{21}\text{N}$.	I.	Found.
			II.
C	86.69	86.49	. .
H	7.98	8.20	. .
N	5.32	. .	5.49

The molecular weight determined in boiling acetone:

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
23.00	1.0645	0.316	250
"	1.5865	0.428	251
Calculated for $\text{C}_{19}\text{H}_{21}\text{N}$,			263

It was extremely difficult to establish the structure of this compound because the cyanogen group does not give any of its usual reactions. That it would be difficult to hydrolyze it could be anticipated from the experiences of E. Fischer¹ and of Victor Meyer² with similarly constituted substances. Fischer succeeded in getting triphenylacetic acid by heating its nitrile to 220° – 228° , with a mixture of concentrated hydrochloric and glacial acetic acids, but similar treatment of this compound gave only unchanged nitrile. Victor Meyer and his pupils found that it is generally possible to transform refractory nitriles into acid amides by protracted boiling with aqueous alcoholic potassium hydroxide. This was tried, but the sole

¹ Ann. Chem. (Liebig), 194, 262.

² *Ibid.*, 250, 157.

effect, after boiling for 6 days, was found to be the elimination of a small quantity of cyanogen as potassium cyanide. After vainly trying Gattermann's¹ and Sudborough's² modifications of Bouveault's method, all attempts at direct hydrolysis were abandoned.

The nitrile was then treated with Grignard's reagent, in the expectation of getting a ketone that could subsequently be transformed into the acid; but even this reaction, which takes place so readily with simpler nitriles, failed. After boiling for a day with methylmagnesium iodide and phenylmagnesium bromide the entire amount of nitrile was, in each case, recovered.

The structure of the substance was finally established by reduction. Ladenburg's method, using sodium in boiling absolute alcohol, proved inefficient, but when boiling amyl alcohol was substituted for ordinary alcohol the nitrile slowly disappeared and no unchanged substance could be detected after adding 15 times the calculated amount of sodium. The alcoholic layer, on distillation with steam, gave a solid that is much less volatile with steam than amyl alcohol. More of this solid was obtained by fractioning the alcoholic distillate under diminished pressure. The solid was purified by crystallization from ligroin. Analysis:

0.1575 gram substance gave 0.5245 gram CO₂ and 0.1312 gram H₂O.

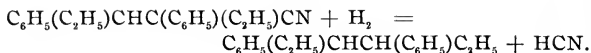
	Calculated for C ₁₈ H ₂₂ .	Found.
C	90.8	90.8
H	9.2	9.3

The substance is 3,4-diphenylhexane. It melts at 92°, boils at 175° (20 mm.) and is readily soluble in organic solvents.

The alkaline solution contained all the cyanogen as potassium cyanide, hence the reduction is represented by the equation:

¹ Ber. d. chem. Ges., 30, 1279.

² *Ibid.*, 28, 917.



Methyldiphenylvaleronitrile, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{CHC}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{CN}$, was made for the purpose of ascertaining whether it would be easier to hydrolyze it than the corresponding ethyl derivative. It crystallizes in prisms, is readily soluble in alcohol and ether, and melts at 99° . Analysis:

0.1311 gram substance gave 0.4160 gram CO_2 and 0.0909 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{19}\text{N}$.	Found.
C	86.74	86.54
H	7.62	7.70

All efforts to hydrolyze the substance were unsuccessful.

Benzyl diphenylvaleronitrile,

$\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{CHC}(\text{CH}_2\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{CN}$.—Victor Meyer and his pupils found it impossible to introduce a benzyl group into benzyl cyanide, in which one hydrogen had previously been replaced by methyl, ethyl, or benzyl. It was of interest, therefore, to determine whether such a group can be introduced by means of the magnesium derivative. It was found that, while the latter reacts more slowly with benzyl bromide than with ethyl iodide, the final result is just as satisfactory, the yield of the new compound being almost the calculated amount. The product of the reaction was poured into water and distilled with steam, to remove excess of benzyl bromide and a small quantity of the ethyl derivative formed from the excess of ethyl bromide used in the preparation of the magnesium derivative. The residue was purified by crystallization from alcohol and benzene. From the latter it crystallized in needles, containing 1 molecule of benzene, which it loses slowly at the ordinary temperature. Analysis:

0.7663 gram substance lost 0.1471 gram at 100° .

	Calculated for $\text{C}_{24}\text{H}_{23}\text{N} \cdot \text{C}_6\text{H}_6$.	Found.
C_6H_6	19.30	19.21

I. 0.1300 gram substance gave 0.4213 gram CO_2 and 0.0844 gram H_2O .

II. 0.4090 gram substance gave 16.7 cc. N at 23° and 753 mm.

	Calculated for $\text{C}_{24}\text{H}_{28}\text{N}$.	I.	Found. II.
C	88.59	88.39	. .
H	7.10	7.21	. .
N	4.31	. .	4.56

The molecular weight determined in boiling acetone :

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
55.0	0.7460	0.074	313
"	1.1505	0.116	300
"	1.8370	0.187	306

Calculated for $\text{C}_{23}\text{H}_{24}\text{N}$, 325

The compound is readily soluble in benzene, acetone and boiling alcohol, sparingly soluble in cold alcohol and ligroin. It melts at 140° .

All of these alkyl derivatives contain two unequal, asymmetrical carbon atoms and are, therefore, capable of existing in two inactive modifications, but only one substance was obtained in each case. It follows that only one magnesium derivative is formed when ethylmagnesium bromide combines with phenylcinnamionitrile, and that the two stereoisomeric diphenylvaleronitriles described above result from the process of decomposing this magnesium derivative with water. It is possible to vary the relative amounts of the isomers, but it has not been feasible, up to this time, to direct the reaction in such a way as to get only one substance.

Benzoyldiphenylvaleronitrile,



The magnesium derivative was treated with an equivalent quantity of benzoyl chloride and the mixture boiled for an hour. The product separated in the solid form when the solu-

tion was poured into ice-water. The reaction is a clean one and, like that with halogen alkyls, gives but one substance, which is obtained in calculated quantity. It was purified by crystallization from alcohol, from which it separated in large needles, melting at 137° . It is readily soluble in chloroform, acetone and boiling alcohol, moderately in cold alcohol and ether, very sparingly in ligroin. Analysis:

0.1520 gram substance gave 0.4748 gram CO_2 and 0.0858 gram H_2O .

	Calculated for $\text{C}_{24}\text{H}_{21}\text{ON}$.	Found.
C	85.00	85.18
H	6.12	6.26

The benzoyl derivative does not reduce a solution of potassium permanganate and it is indifferent to bromine. It is very easily hydrolyzed both by acids and bases, the sole products, in each case, being the solid diphenylvaleronitrile and benzoic acid. Although it is not feasible, at present, to distinguish between the two possible formulas written above, the first seems the more probable in view of the relatively low melting point and the fact that only one nitrile is formed on hydrolysis.

The acid $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)(\text{CN})\text{COOH}$ or

$\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5) : \text{C} : \text{NCO}_2\text{H}$.—The magnesium derivative absorbed dry carbon dioxide rapidly and passed into a crystalline solid that was insoluble in ether. This was thoroughly washed with anhydrous ether, then suspended in ice-water and cautiously acidified with iced hydrochloric acid. The organic acid separated as an oil, and all efforts to solidify it, or get it in any other form suitable for analysis, failed. That it is a single substance is certain, because it breaks down when warmed and gives, as the only products, carbon dioxide and solid diphenylvaleronitrile. At low temperatures the acid is fairly stable. After standing in an ice chest for several days it still dissolved completely in a solution of sodium bicarbonate. At the ordinary temperature it slowly gives off carbon dioxide and it decomposes instantaneously when dropped into boiling water. The salts are

still less stable than the acid. The solution in sodium bicarbonate became milky with separated nitrile when it was evaporated at 0° , in a vacuum, and when the oil was treated with potassium hydroxide it passed into the solid nitrile, apparently without previously going into solution.

3,4-Diphenylhexanone-2, $C_2H_5CH(C_6H_5)CH(C_6H_5)COCH_3$.—Diphenylvaleronitrile (115°) readily reacts with methylmagnesium iodide. The reaction was studied for the purpose of ascertaining whether it would yield two stereoisomeric ketones. This was found to be the case. One of the ketones separated in the solid form when the product of the reaction was poured into iced hydrochloric acid. The other remained in the ethereal solution and, on evaporation, deposited as an oil. The solid was purified by crystallization from alcohol. It was obtained in stout needles, melting at 116° . It is readily soluble in ether and acetone, moderately in cold alcohol, sparingly in ligroin.

By fractional distillation, under diminished pressure, the oil was separated into two substances, the ketone already described and a new compound that solidified in the receiver. The latter, after crystallization from ligroin, melted at 56° . The analyses show that the substances are isomeric.

I. 0.1443 gram substance (116°) gave 0.4547 gram CO_2 and 0.1012 gram H_2O .

II. 0.1313 gram substance (56°) gave 0.4120 gram CO_2 and 0.09279 gram H_2O .

	Calculated for $C_{18}H_{20}O$.	I.	Found.	II.
C	85.71	85.82		85.60
H	7.93	7.76		7.86

The oily modification of diphenylvaleronitrile was also treated with methylmagnesium iodide and, as was to be expected, gave a mixture of the same two ketones.

Diphenylvalerophenone, $C_1H_5CH(C_6H_5)CH(C_6H_5)COC_6H_5$.—Two isomeric ketones are also obtained when either the solid or the oily diphenylvaleronitrile is added to a solution of phenylmagnesium bromide. The high-melting ketone crystal-

lizes in needles, melting at 170° . It was purified by crystallization from a mixture of chloroform and alcohol. It is readily soluble in acetone and chloroform, sparingly in alcohol and ether.

The low-melting ketone crystallizes in plates, melting at 92° . It is readily soluble in alcohol and ether, sparingly in ligroin. It was purified by crystallization from a mixture of ligroin and ether. Analyses :

I. 0.1375 gram substance (170°) gave 0.4443 gram CO_2 and 0.0886 gram H_2O .

II. 0.1234 gram substance (92°) gave 0.3970 gram CO_2 and 0.0783 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{22}\text{O}$.	I.	Found. II.
C	87.93	88.05	87.74
H	7.00	7.16	7.05

In view of the results just described and those recorded in an earlier paper,¹ it is probable that a product obtained by Grignard's reaction always contains all possible racemic modifications.

II. *Phenylcinnamionitrile and Phenylmagnesium Bromide.*

This reaction, as stated in the introduction, always gives rise to two products : triphenylpropionitrile and benzaldehydo-benzoin.

There is no evidence of action when the reagents are brought together at the ordinary temperature ; the solid nitrile dissolves in the ethereal solution of the magnesium compound without production of color and without evolution of heat and, if the clear solution is immediately poured into ice-water, all of the nitrile is recovered. The reaction proceeds slowly, however, even in an ice chest and becomes complete in 4 to 6 weeks. The product, on treatment with ice-water, gives about 20 per cent of unsaturated ketone. The remainder is triphenylpropionitrile.

In a boiling solution of the magnesium compound, the unsaturated nitrile immediately gives rise to a blood-red color

¹ THIS JOURNAL, 28, 153.

that slowly disappears again on continued boiling. The reaction is complete after 2-3 hours and the product, treated in the usual way, gives 30-40 per cent of unsaturated ketone.

It is difficult to separate the mixture of benzaldesoxybenzoin and triphenylpropionitrile. The best results were obtained as follows: The product of the reaction, diluted with 2-3 times its volume of ether, is poured into iced hydrochloric acid contained in a separating funnel. The magnesium derivative of the nitrile is decomposed at once and most of the nitrile dissolves in the ether, while the magnesium derivative that yields the unsaturated ketone passes into a thick paste which adheres to the ice and the walls of the funnel. By drawing off the ethereal solution immediately, a fairly good separation is obtained.

The paste dissolves slowly when it is shaken with ether and dilute hydrochloric acid. The ethereal solution, on evaporation and dilution with alcohol, first deposits the high-melting modification of benzaldesoxybenzoin and then a small quantity of oil. The ketone was identified by analysis and comparison with a specimen made from benzil. The oil was added to the ethereal solution obtained directly from the magnesium compound. This solution, on evaporation, left an oil that solidified, almost completely, on standing. The solid was recrystallized from methyl alcohol until it melted sharply at 102° . The analysis and reactions given below show that it is triphenylpropionitrile.

The oily residues that accumulated from the mother liquors were dissolved in ether, the solution dried with sodium sulphate and fractioned under diminished pressure. The only substances obtained, after removing small quantities of phenyl bromide and diphenyl, were the two compounds already mentioned.

Triphenylpropionitrile, $(\text{C}_6\text{H}_5)_2\text{CHCH}(\text{C}_6\text{H}_5)\text{CN}$, prepared as just described, crystallizes in plates that melt at 102° . It is readily soluble in alcohol and ether, moderately in methyl alcohol, sparingly in ligroin.

0.1496 gram substance gave 0.4890 gram CO_2 and 0.0935 gram H_2O .

	Calculated for $\text{C}_{21}\text{H}_{17}\text{N}$.	Found.
C	88.26	88.21
H	6.01	6.20

Triphenylpropionamide, $(\text{C}_6\text{H}_5)_2\text{CHCH}(\text{C}_6\text{H}_5)\text{CONH}_2$, was obtained by heating the nitrile to 160° , for 4 hours, with concentrated hydrochloric acid. The small quantity of acid formed at this temperature was removed with sodium carbonate and the residue crystallized from aqueous alcohol. The amide separated in needles, melting at 213° . It is readily soluble in alcohol, moderately in ether, very slightly in boiling water. Analysis :

0.1423 gram substance gave 0.4333 gram CO_2 and 0.0345 gram H_2O .

	Calculated for $\text{C}_{21}\text{H}_{19}\text{ON}$.	Found.
C	83.72	83.44
H	6.33	6.55

By heating the amide at 200° with concentrated hydrochloric acid, it was easy to hydrolyze it to triphenylpropionic acid. This was identified by comparison with a specimen made by saponifying the ester.

Ethyltriphenylpropionitrile, $(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{CN}$.—Ethyl iodide was added to a solution of the magnesium derivative obtained with phenylmagnesium bromide, the mixture boiled for 2 hours, and the product separated as described under triphenylpropionitrile. Two substances were obtained : Benzaldesoxybenzoin and a new compound which was purified by crystallization from alcohol and ligroin. Analysis :

0.1220 gram substance gave 0.3964 gram CO_2 and 0.0755 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{21}\text{N}$.	Found.
C	88.74	88.58
H	6.74	6.95

Ethyltriphenylpropionitrile is readily soluble in alcohol and

ether, moderately in boiling ligroin. It was obtained in needles, melting at 134° . No change took place when the substance was heated to 200° with concentrated hydrochloric acid.

III. Experiments with Cinnamonnitrile and β -Phenylcinnamonnitrile.

Cinnamonnitrile reacts very readily both with methylmagnesium iodide and with phenylmagnesium bromide. Red, intermediate compounds are formed, but these disappear almost immediately. When the solution obtained with methylmagnesium iodide was treated in the usual way, it gave a dark brown oil. A part of this was tested for nitrogen, which proved to be absent, showing that the cyanogen group is involved in the reaction. The remainder of the oil was repeatedly extracted with low-boiling ligroin. This, on evaporation, deposited a pale yellow, crystalline solid, melting at 42° . A small quantity of the solid was dissolved in alcohol and treated with a few drops of benzaldehyde and sodium hydroxide. In a short time dibenzalacetone, melting at 112° , began to separate, proving that the original substance is benzalacetone. The yield of the unsaturated ketone was small—less than 60 per cent of the calculated amount.

The mixture obtained with phenylmagnesium bromide, treated like that obtained from methylmagnesium iodide, gave about 68 per cent of benzalacetophenone. The residue, insoluble in ligroin, was boiled with an alkaline permanganate solution until no further reduction took place. Any product formed by 1,4-addition of phenylmagnesium bromide to cinnamonnitrile would be oxidized to β,β -diphenylpropionic acid by this procedure. The only organic compound obtained was benzoic acid, showing that the reaction involves only the cyanogen group.

The result obtained in a single experiment carried out with β -phenylcinnamonnitrile indicates that this substance reacts like cinnamonnitrile. The only product obtained with phenylmagnesium bromide was β -phenylbenzalacetophenone, which

was identified by comparison with a specimen on hand. The yield was 68 per cent of the calculated amount.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
January, 1906.

Contributions from the Chemical Laboratory of Case School of Applied Science.
XLVI.—ON THE COMPOSITION OF PETROLEUM.

BY CHARLES F. MABERY.

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS
IN CANADIAN PETROLEUM.¹

BY CHARLES F. MABERY AND WILLIAM O. QUAYLE.

In a paper published some time ago by one of us (Mabery) on a preliminary examination of Canadian petroleum,² it was stated that 225 liters of sulphur oil from Canadian burning oil was in process of distillation for the purpose of separating the individual sulphur constituents. On account of the pressure of other lines of work, study of those distillates was delayed, but it has been resumed at intervals until the results described in this paper were obtained.

On returning to this work it seemed worth while to ascertain first whether the oil selected really represented constituents of crude petroleum, or whether it consisted, to a greater or less extent, of decomposition products incident to the process of refining. Since the question of decomposition could be determined in sulphur petroleum from any source, a quantity of crude oil from the Lima, Ohio, field was distilled *in vacuo* and the distillate, corresponding to that from which burning oil is prepared, carefully separated and agitated thoroughly with alcoholic mercuric chloride, for the purpose of precipitating the sulphur compounds. The oil was next agitated vigorously with ordinary sulphuric acid, the acid sludge drawn off and diluted with water, carefully avoiding heat so far as possible.

As usual, a dark red oil separated above the solution, but it

¹ The sulphur derivatives of the hydrocarbons described in this paper are evidently members of a new series, differing essentially in composition, physical properties and chemical relations from any of the well-known series of sulphur compounds. For this new series I suggest the name Thiophane. C. F. M.

² THIS JOURNAL, 13, 89 (1891).

lacked the heavy sulphurous odor characteristic of sludge as it is ordinarily separated from sulphur petroleum. The odor of this oil resembled that of sludge after the sulphur compounds had been removed, and it showed still greater similarity in its behavior toward bromine, with which it readily united with the evolution of heat, and the formation of an addition product heavier than water, precisely similar to the behavior of sludge products. The precipitate with mercuric chloride resembled, in all respects, the characteristic products which are so useful in separating the sulphur compounds.

As further evidence of the presence of unsaturated hydrocarbons in this oil, a portion of the oil precipitated from sulphuric acid was heated with concentrated hydrobromic acid to 100° , and the product fractionated *in vacuo* to collect, in a smaller limit, the bromine addition product. It was not intended to prepare an individual bromine derivative sufficient for analysis, since this would have been impossible with the small amount to be obtained in this manner, but only to be sure that an addition product with hydrobromic acid could be formed. The higher vacuum distillate gave an abundant reaction for bromine after heating with lime, showing that addition of the acid had taken place. The results of these experiments are described in full, that there may be no misapprehension concerning the source of the sulphur compounds and unsaturated hydrocarbons which will be described in this paper. They confirm the results of similar experiments described in the former paper.

In continuing the distillation of the 225 liters of crude sulphur oil, with the aid of the apparatus elsewhere described, the distillates were carried through entire up to 250° (50 mm.) at first within 5° , during 4 distillations. The lower fractions were then continued within single degree fractions until the lower portions could be distilled under atmospheric pressure. It was not possible to accomplish in this manner more than a general separation, since all the distillates were mixtures, yet the value of the great amount of tedious labor was shown after the separation of the individual constituents, of which the greater portion distilled at approximately the same tempera-

tures as the original distillates; and although it seemed a great expenditure of effort to distil such a large volume of oil in quantities of 10 liters, the capacity of the porcelain still employed, and to continue the distillation of the entire quantity, this seemed to be the only available method for the separation of these peculiar bodies from the crude oil. When first collected, all the fractions were nearly colorless, but on standing they turned dark red, especially those with higher boiling points. The fractions collected below 125° (50 mm.) were found to be exceedingly unstable. On standing from 6 months to 2 years, some of these distillates deposited very dark, heavy oils, doubtless formed from unstable unsaturated hydrocarbons, terpenes, or sulphur compounds by polymerization.

In separating the constituents of the vacuum distillates, we followed, in general, the method described in a former paper. Three or four hundred grams of the oil were shaken in a large flask with an excess of an alcoholic solution of mercuric chloride, which gave a heavy precipitate, crystalline in the lower fractions, a thick, viscous mass in the less volatile and a heavy, oily deposit in the vacuum distillates above 160° . There invariably separated above the alcohol a lighter oil, which contained no sulphur, or at most, analysis showed less than 0.5 per cent. Upon diluting the alcohol more lighter oil collected, which doubtless has a different composition from the other, since, as will appear later, it showed essentially different properties.

In recovering the sulphur compounds from the mercuric chloride precipitates, after thoroughly washing with alcohol and very volatile gasolin, the precipitate was decomposed by hydrogen sulphide, in presence of a considerable volume of alcohol, the mercuric sulphide separated by filtration, washed with alcohol and the alcohol largely diluted. For the most part the lighter oil separated, some remaining in suspension, which collected after standing a short time. With all possible care in washing the mercuric chloride precipitate, a single precipitation was never sufficient to remove all the sulphur-free oil. The percentages of sulphur in the individual sulphur compounds invariably came from 1 to 3 per cent too low, how-

ever long they were fractioned, until they were a second time converted into the mercuric chloride compound and again separated by hydrogen sulphide. Upon diluting a second time, usually another portion of the sulphur-free oil collected, or remained in suspension and, after sufficient fractioning, the percentage of sulphur then corresponded to the value theoretically required.

It has already been explained that the vacuum fractions of the crude sulphur oil, before the separation of its constituents, is a mixture of an unsaturated hydrocarbon, a sulphur compound and another hydrocarbon of a series not determined. More attention will be given later to the sulphur-free oils. All the portions selected for the separation of these constituents had previously been fractionated from 4 to 20 times, for the most part *in vacuo*, and since the sulphur oil from any particular fraction has corresponded in boiling point to that of the fraction before separation, it has been possible to select, from the great number of first fractions, those which should give the bodies desired, thereby saving much time and unnecessary labor in searching for the individual constituents.

After the second precipitation from the mercuric chloride compound, a few distillations *in vacuo*, with the aid of a bead column, in a long-necked flask, have been sufficient to bring together, for the most part within 1° or 2° , the sulphur compound desired. For the separation without decomposition of the sulphur oils boiling above 130° , distillation *in vacuo* has been indispensable. Doubtless exclusion of air, as well as the reduction in boiling points, especially of the higher members, is essential.

The most volatile vacuum distillates, 40° – 50° , were subjected to 8 additional distillations within limits of 2° , and 300 cc. of these distillates was agitated with an excess of alcoholic mercuric chloride. A part of the oil was immediately converted into a crystalline precipitate, and the sulphur-free oil, which formed the greater part of the oil taken, remained entirely in solution and was separated by dilution. After decantation of the alcoholic solution, the crystalline precipitate was well

washed with alcohol and light gasolin, and decomposed by hydrogen sulphide in presence of alcohol.

For complete removal of the sulphur-free oil the mercuric chloride compound was again formed, washed and the sulphur oil separated by hydrogen sulphide. Unfortunately, the larger portion of the sulphur oil was accidentally lost, but the remainder was fractioned, so far as possible, until, finally, it showed a tendency to collect at 125° – 130° .

The percentage of sulphur found in this product was 27.12; required for the sulphur compound, $C_6H_{12}S$, 27.60. The crystalline condition of this substance is characteristic of the alkyl sulphides; but all the sulphur bodies we have separated from petroleum are viscous oils that could not be solidified, except the more volatile sulphur compounds such as were separated from Ohio petroleum, which were crystalline.

The following series of sulphur compounds, which have been identified by analysis and shown to have the composition of the general formula $C_nH_{2n}S$, do not represent any series known. They are not members of the ethylene sulphide series, as shown by their reactions and very high specific gravity. In empirical composition they correspond to hydrothiophenes, which have not been synthetically prepared.

Heptyl Thiophane.

Fraction 158° – 160° , $C_7H_{14}S$.

The heptyl sulphur compound was identified in the vacuum distillate 71° – 73° (50 mm.) seventh distillation. After precipitation with alcoholic mercuric chloride, and thorough washing with alcohol and light gasolin, the thick, viscous oil was decomposed with hydrogen sulphide, in the presence of alcohol. The oil that separated on dilution of the alcohol was fractionated *in vacuo* until it distilled at 74° – 76° (50 mm.) and at 158° – 160° (750 mm.). A determination of its sp. gr. at 20° gave 0.8878. Analysis gave percentages of carbon, hydrogen and sulphur required for the formula $C_7H_{14}S$. Carbon and hydrogen were determined by combustion in lead chromate, the sulphur by combustion in oxygen.

I. 0.1749 gram oil gave 0.4141 gram CO_2 and 0.1748 gram H_2O .

II. 0.1666 gram oil gave 0.3071 gram BaO_4 .

	Calculated for $\text{C}_7\text{H}_{14}\text{S}$.	I.	Found.	II.
C	64.63	64.59	.	.
H	10.76	11.18	.	.
S	24.61	.	.	25.31

Octyl Thiophane.

Fraction 167° – 169° , $\text{C}_8\text{H}_{16}\text{S}$.

For the separation of the next sulphur homologue the large quantity of distillate was selected that collected at 79° – 81° (50 mm.) after the seventh distillation. One hundred cc., with the treatment described above, yielded 20 cc. of the sulphur compound, that distilled constant at 81° – 83° (50 mm.) and at 167° – 169° under atmospheric pressure. The sp. gr. of this oil was found to be 0.8929 at 20° . Analyses :

I. 0.1666 gram oil gave 0.4057 gram CO_2 and 0.1671 gram H_2O .

II. 0.1391 gram oil gave 0.2282 gram BaSO_4 .

	Calculated for $\text{C}_8\text{H}_{16}\text{S}$.	I.	Found.	II.
C	66.67	66.46	.	.
H	11.11	11.22	.	.
S	22.22	.	.	22.53

Isooctyl Thiophane.

Fraction 183° – 185° , $\text{C}_8\text{H}_{16}\text{S}$.

A large amount of distillate collected at 97° – 99° (50 mm.), at the end of the seventh distillation, that gave, by analysis, the same empirical formula as the sulphur compound previously described. The term isooctyl is applied to this compound to distinguish it from its isomer. Upon treatment with mercuric chloride and second precipitation, a large amount of sulphur-free oil collected on dilution of the alcohol, and analysis showed that this constituent was completely removed by the second treatment. After fractionating *in vacuo* this product collected to the extent of 15 cc. at 94° – 96° (50 mm.), and dis-

tilled, with some decomposition, at 183° – 185° , atmospheric pressure. Sp. gr. at 20° , 0.8937. Analyses :

I. 0.1458 gram oil gave 0.3592 gram CO_2 and 0.1470 gram H_2O .

II. 0.1561 gram oil gave 0.3814 gram CO_2 and 0.1575 gram H_2O .

III. 0.2670 gram oil gave 0.4183 gram BaSO_4 .

	Calculated for $\text{C}_8\text{H}_{16}\text{S}$.	I.	Found. II.	III.
C	66.67	67.19	66.16	. .
H	11.11	11.27	11.29	. .
S	22.22	21.52

It will be observed that the last two compounds have the same empirical composition, but differ by 16° or more in boiling points, and differ also in specific gravity. It will also be observed that they agree closely in boiling points with butyl and isobutyl sulphides ; but they differ widely from the latter in specific gravity : butyl sulphide, 0.8523 at 0° ; isobutyl sulphide, 0.8363 at 10° , and in other properties.

Nonyl Thiophane.

Fraction 139° – 195° $\text{C}_9\text{H}_{18}\text{S}$.

A portion of the distillate that collected in considerable quantity at 106° – 108° (50 mm.) was treated in the same manner as previously described, with two precipitations for the separation of the sulphur compound. The product was fractionated *in vacuo* until it collected, for the most part, at 106° – 108° (50 mm.). Under atmospheric pressure it boiled at 193° – 195° , and gave, as its sp. gr. at 20° , 0.8997. Analyses :

I. 0.1927 gram oil gave 0.4852 gram CO_2 and 0.2033 gram H_2O .

II. 0.1547 gram oil gave 0.2210 gram BaSO_4 .

	Calculated for $\text{C}_9\text{H}_{18}\text{S}$.	I.	Found. II.
C	68.35	68.68	. .
H	11.40	11.80	. .
S	20.25	. .	19.62

*Decyl Thiophane.*Fraction 207°-209°, $C_{10}H_{20}S$.

From the vacuum distillate, 114°-115° (50 mm.) after the seventh distillation, a sulphur oil was prepared by two precipitations with mercuric chloride, that collected, after fractioning some time *in vacuo*, for the most part, at 114°-116° (50 mm.). It distilled at 207°-209° (750 mm.) and gave sp. gr., at 20°, 0.9074. Analyses:

I. 0.2323 gram oil gave 0.5904 gram CO_2 and 0.2453 gram H_2O .

II. 0.1981 gram oil gave 0.5078 gram CO_2 and 0.2094 gram H_2O .

III. 0.1654 gram oil gave 0.2240 gram $BaSO_4$.

IV. 0.1760 gram oil gave 0.2407 gram $BaSO_4$.

	Calculated for $C_{10}H_{20}S$.	I.	II.	Found. III.	IV.
C	69.77	69.33	69.92
H	11.62	11.32	11.82
S	18.60	18.59	18.78

*Undecyl Thiophane.*Fraction 128°-130° (50 mm.), $C_{11}H_{22}S$.

The vacuum distillate, 135°-145° (50 mm.), was selected for the separation of the next homologous sulphur compound. A thick, tarry mass was formed by precipitation with mercuric chloride, which gave the pure sulphur oil by a second precipitation. The viscosity of the compounds with mercuric chloride was found to increase with increase in molecular weights of the sulphur oils. Three hundred grams of the first distillate, 135°-145°, fourth distillation, gave, after the second precipitation with mercuric chloride, 122 grams insoluble in alcohol, 60 grams in the alcoholic solution, and 84 grams of the sulphur oil. Without further purification, the latter gave 16.08 per cent sulphur. After continued fractioning *in vacuo* the sulphur oil collected, for the most part, at 128°-130° (50 mm.). Analyses:

I. 0.1793 gram oil gave 0.4669 gram CO_2 and 0.1896 gram H_2O .

II. 0.2064 gram oil gave 0.5334 gram CO_2 and 0.2122 gram H_2O .

III. 0.1921 gram oil gave 0.2411 gram BaSO_4 .

	Calculated for $\text{C}_{11}\text{H}_{22}\text{S}$.	I.	Found. II.	III.
C	70.98	71.01	70.71	. .
H	11.82	11.82	11.50	. .
S	17.20	17.24

The sp. gr. of this sulphur oil was found to be 0.9147, at 20° . Particular attention was given to the purification of this product, to be certain of the series as shown by the most careful analysis. In addition to the determinations given above that demonstrate its composition, the following additional analyses were made of different preparations: carbon found, 70.73, 70.74; hydrogen in the same combustions, 11.48, 11.95; sulphur, 17.28, 17.05, 17.10.

The portions of the original sludge oil, called sulphur-free oils to distinguish them from the sulphur oils, have contained from 0.1 to 0.3 per cent of sulphur, and it has been assumed that the small proportion of sulphur indicated a little of the sulphur compound not precipitated by mercuric chloride. That the part collecting above the alcohol, after precipitation, is a different product from the part remaining in solution in alcohol is shown by the difference in specific gravity. For example, the distillate 136° – 145° , from which the oil $\text{C}_{11}\text{H}_{22}\text{S}$ was obtained, gave an oil insoluble in alcohol with sp. gr. 0.8412; but the sp. gr. of the portion in solution was found to be 0.8107. Similar differences appeared in oils associated with other thiophanes. Since the specific gravity of any one of the principal hydrocarbons in Canadian petroleum corresponding in boiling point with these bodies is smaller than the specific gravity of the sulphur oils, and since hydrocarbons are sparingly soluble in sulphuric acid and alcohol, the bodies under examination cannot be the principal petroleum hydrocarbons. Then the odors of both the substances soluble and insoluble in alcohol are unlike that of any of the hydrocarbons—very pungent, resembling the terpenes. Further study will be necessary to identify these peculiar bodies.

*Quatdecyl Thiophane.*Fraction 266°–268°, $C_{14}H_{28}S$.

This sulphur oil was separated from the distillate 160°–170° (50 mm.), fourth distillation. After the second precipitation and decomposition by hydrogen sulphide, 400 grams of the sludge distillate gave 75 cc. of a yellow oil that collected, for the greater part, at 168°–170° (50 mm.), after extended fractioning. It collected at 266°–268° (750 mm.). Its sp. gr. at 20° was found to be 0.9208. Analyses:

I. 0.1859 gram oil gave 0.5010 gram CO_2 and 0.2109 gram H_2O .

II. 0.2290 gram oil gave 0.2336 gram $BaSO_4$.

	Calculated for $C_{14}H_{28}S$.	I.	Found.	II.
C	73.68	73.52	.	.
H	12.28	12.69	.	.
S	14.04	.	.	14.02

*Sexdecyl Thiophane.*Fraction 283°–285°, $C_{16}H_{32}S$.

From 400 cc. of the first vacuum distillate 170°–180° (50 mm.), after the second precipitation with mercuric chloride and long-continued distillation, 28.5 grams of the sulphur oil collected at 184°–186°, which distilled, with some decomposition, at 283°–285° (750 mm.). Its sp. gr. was found to be 0.9222. Analyses:

I. 0.2148 gram oil gave 0.5934 gram CO_2 and 0.2380 gram H_2O .

II. 0.1850 gram oil gave 0.1683 gram $BaSO_4$.

	Calculated for $C_{16}H_{32}S$.	I.	Found.	II.
C	75.00	75.36	.	.
H	12.50	12.40	.	.
S	12.50	.	.	12.49

*Octadecyl Thiophane.*Fraction 290°–295°, $C_{18}H_{36}S$.

From 350 grams of the vacuum distillate 191°–210° (50

mm.), alcoholic mercuric chloride gave a very thick, viscous precipitate, from which was obtained, after the second precipitation, 50 grams of a dark colored oil that collected, after continued distillation *in vacuo*, nearly colorless, for the most part, at 198° – 202° . Under atmospheric pressure this oil distilled, with some decomposition, at 290° – 295° ; sp. gr., at 20° , 0.9235. The values obtained by analysis corresponded to the formula $C_{18}H_{36}S$.

I. 0.2005 gram oil gave 0.5602 gram CO_2 and 0.2214 gram H_2O .

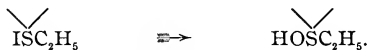
II. 0.1937 gram oil gave 0.1634 gram $BaSO_4$.

III. 0.2011 gram oil gave 0.1636 gram $BaSO_4$.

	Calculated for $C_{18}H_{36}S$.	I.	Found. II.	III.
C	76.06	76.22	. .	
H	12.67	12.35
S	11.27	. .	11.57	11.18

We have made no attempts toward the separation of sulphur compounds with higher molecular weights, but there is no doubt that higher homologues are contained in the less volatile distillates which we have separated from the original oil. It is probable that intermediary members of this series are contained in the distillates examined, and that they might be identified in larger quantities of material.

As has been shown in the method of preparation, the thiophanes combine readily with alcoholic mercuric chloride to form viscous oils. They also form addition products with chlorplatinic acid, which are heavy, viscous oils. When heated in a sealed tube with ethyl iodide, addition products are formed which crystallize in small prisms, $-C_nH_{2n}S$, C_2H_5I . These addition products form alkaline hydroxides when warmed with silver oxide and water :



Bromine exerts a characteristic action on these sulphur compounds. Immediately, when they come in contact, combination follows with almost explosive violence, and copious evolu-

tion of hydrobromic acid, in equivalent amounts to the bromine added. It is wholly unlike the behavior of unsaturated hydrocarbons with bromine. Probably part of the bromine combines with the sulphur, but the evolution of hydrobromic acid begins immediately, doubtless due to the ready replacement of the methylene hydrogen atoms.

The thiophanes still further resemble the well-known series of sulphur derivatives in their behavior toward oxidation. The formation and properties of the sulphones will be described later.

In addition to the analytical data that establish the composition of the thiophanes, we have determined their indices of refraction, and the corresponding molecular refraction verifies the formulas given by analysis.

Indices of Refraction of the Thiophanes.

Many attempts were made, with different solvents, to determine the molecular weights of the sulphur compounds in Canadian petroleum, but no concordant values could be obtained, even with the same substance and the same solvent.

Better success, however, was reached in ascertaining the indices of refraction, but since the values for sulphur in organic compounds have not been determined with the same certainty as in the case of carbon, hydrogen and oxygen, some attention was given to verifying this constant.

The index of refraction found by Nasini for ethyl sulphide was 1.44233; for ethyl mercaptan, 1.43055; and for ethyl disulphide, 1.50633.

Assigning the accepted values to carbon and hydrogen, the calculated value for sulphur becomes, for ethyl sulphide, 7.98; for ethyl mercaptan, 7.81; and for ethyl sulphide, 8.03. In determining the value of sulphur in ethyl mercaptan, we found the angle to be $49^{\circ} 24'$, which corresponds to the index 1.4323, and the calculated value for sulphur is 7.89.

Isobutyl sulphide gave us 1.4585 as its index of refraction, calculated from the observed angle $44^{\circ} 57'$; the corresponding molecular refraction is 46.85. Assigning the accepted values to carbon and hydrogen, the difference is the value of sulphur,

7.98, the same as the value calculated from Nasini's index of ethyl sulphide.

The index assigned to thiophen is 1.5268, which gives as its molecular refraction, 24.12, leaving a value for sulphur 6.53. Thiophen is assumed to have two sets of double bonds. The petroleum sulphur compounds under consideration, although doubtless possessing a ring structure, apparently do not contain carbon atoms connected by double linkage. We have, therefore, considered it safe to use the value 7.98 for sulphur, and the following molecular refraction for the petroleum sulphur compounds were calculated on the basis of this value :

Heptyl Thiophane.

The fraction 74° – 76° (50 mm.), which proved to contain heptyl thiophane, gave as its index of refraction 1.468, corresponding to the following molecular refraction :

Calculated for $C_7H_{14}S$.	Found.
40.15	40.82

Octyl Thiophane.

From the fraction 83° – 85° (50 mm.) was separated octyl thiophane. Its index of refraction was found to be 1.4860, and its molecular refraction :

Calculated for $C_8H_{16}S$.	Found.
44.75	44.91

Nonyl Thiophane.

Nonyl thiophane was found to be the principal constituent of the fraction 106° – 108° (50 mm.). It gave, as its index of refraction, 1.4746, from which was calculated its molecular refraction :

Calculated for $C_9H_{18}S$.	Found.
49.35	49.50

Decyl Thiophane,



The index of refraction of the distillate 114° – 116° , from

which was separated decyl thiophane, we found to be 1.4766. Its molecular refraction was calculated as follows :

Calculated for	Found.
$C_{10}H_{20}S$.	
53.94	53.60

Undecyl Thiophane.

Undecyl thiophane was found in the fraction 130° – 135° (50 mm.). We found its index of refraction to be 1.480, and its molecular refraction :

Calculated for	Found.
$C_{11}H_{22}S$.	
58.54	58.53

Quatdecyl Thiophane.



The fraction 168° – 170° gave quatdecyl thiophane. Its index of refraction, 1.4892, corresponded to the molecular refraction :

Calculated for	Found.
$C_{14}H_{28}S$.	
72.33	71.61

Sexdecyl Thiophane.

This sulphur compound was found in the fraction 184° – 186° (50 mm.). Its index of refraction proved to be 1.4903, from which its molecular refraction was calculated :

Calculated for	Found.
$C_{16}H_{32}S$.	
81.52	80.44

The index of refraction of octodecyl thiophane was found to be 1.4977, but the molecular refraction calculated from this value and its sp. gr. 0.9625 at 20° , gave a value different by 4 units from the calculated molecular refraction.

Oxidation Products of the Thiophanes.

Appreciating the importance of oxidation products in ascertaining the composition of the thiophanes, we have tried very thoroughly the action of oxidation agents, nitric acid, chromic acid and potassium permanganate. These sulphur compounds

absorb oxygen with great readiness, and the reaction must be carefully controlled to prevent ultimate oxidation to sulphuric acid. It was not found possible to limit the oxidation to the formation of the sulphoxide, since the sulphone seems to be the more stable condition. Nitric acid readily oxidizes the sulphur with an extremely violent reaction, but, apparently, also forms nitro derivatives, since the products contain nitrogen.

Chromic acid oxidizes the sulphur readily, with some danger that the reaction proceeds to ultimate oxidation. Potassium permanganate, in either alkaline or acid solution, readily effects the change with little danger of the formation of sulphuric acid. After careful study of the conditions, it was found that the largest yield of oxidation product was obtained by adding slowly, to the oil, 1.5 times the calculated weight of permanganate, dissolved in 30 times its weight of water, keeping the solution cold. With efficient cooling, the permanganate can be added as rapidly as it is decolorized. After the reaction was complete the precipitated manganic oxide was filtered and the solution distilled with steam, which carried over any unoxidized sulphur compound, leaving behind the oxidation product. When carefully conducted, the solution shows no sulphuric acid. From the residue of the steam distillation the oxidation product was extracted with ether and the ether evaporated, leaving a thick, heavy oil, which increased in viscosity with increase in molecular weight. In several instances we dissolved the precipitated manganic oxide by saturating with sulphurous oxide and extracted with ether. When the oxidation is complete this is the easier method; but distillation with steam insures the removal of any decomposition products.

The action of oxidizing agents showed a wide difference in deportment between the sulphur compounds from Canadian petroleum and sulphides synthetically prepared. For example, synthetic isoamylsulphide, allowed to stand with concentrated nitric acid, showed vigorous reaction only after several minutes, with evolution of heat. After the reaction ceased heat was applied and water added. The oxidation product

collected above the water and partly dissolved. Only a trace of sulphuric acid was found in the solution. On treating the sulphur compounds from Canadian petroleum in the same manner, the reaction was much more vigorous, with immediate evolution of heat. The product formed a thick oil, heavier than water, and much sulphuric acid was formed, but the oxidized oil contained much sulphur, showing that it consisted, in part, of an oxidized sulphur compound. This difference in the action of nitric acid is pretty conclusive proof that the sulphur compounds under consideration are not alkyl sulphides, nor, indeed, members of any other well-known series. It is in accordance with the observation that the hydro-ring compounds, the methylenes, are less stable toward reagents than the aromatic or paraffin compounds.

Hexyl Thiophane Sulphone.

The presence of hexyl thiophane was indicated in the fraction 125° – 130° (atmospheric pressure), although it was not separated in a pure form. In attempting to prepare the sulphone, the fraction 55° – 57° (50 mm.) was treated, as described above, with potassium permanganate. Oxidation was rapid, even when cooled to 0° . In this instance, after dissolving the manganic oxide in sulphurous acid, the solution was evaporated to dryness and the residue extracted with anhydrous ether. Evaporation of the ether left a thick, viscous oil with a sweetish taste and odor, with no reaction for sulphuric acid. While the analytical values obtained indicated that the hexyl compound was contaminated with a higher homologue, it is evident that hexyl thiophane was the principal constituent. Analysis :

C, 49.39 ; H, 8.47 ; S, 19.02. Required for $C_6H_{12}SO_2$: C, 48.64 ; H, 8.11 ; S, 21.62.

Heptyl Thiophane Sulphone, $C_7H_{14}SO_2$.

The oxidation of heptyl thiophane was conducted as described above. After neutralizing with sodium carbonate and evaporating to dryness, the residue was extracted with anhy-

drous ether. No sulphuric acid was formed by the oxidation. Analysis :

I. 0.1992 gram substance gave 0.3801 gram CO_2 and 0.1531 gram H_2O .

II. 0.1628 gram substance gave 0.2279 gram BaSO_4 .

	Calculated for $\text{C}_7\text{H}_{14}\text{SO}_2$.	I.	Found.	II.
C	51.86	52.05		. .
H	8.64	8.59		. .
S	19.75	. .		19.23

This sulphone formed a very thick, heavy oil. Its sp. gr. was found to be 1.1138 at 20° .

Octyl Thiophane Sulphone,



Fifty grams of the fraction $87^\circ\text{--}89^\circ$, identified as octyl thiophane, was oxidized carefully at 0° . After dissolving the manganic oxide and distilling with steam, 36 grams of a heavy oil separated, with no formation of sulphuric acid. After neutralizing with sodium carbonate, evaporating to dryness and extracting with ether, this oil gave, as its sp. gr. at 20° , 1.1142. Analysis :

I. 0.1697 gram substance gave 0.3385 gram CO_2 and 0.1368 gram H_2O .

II. 0.2038 gram substance gave 0.2702 gram BaSO_4 .

	Calculated for $\text{C}_8\text{H}_{16}\text{SO}_2$.	I.	Found.	II.
C	54.55	54.41		. .
H	9.11	9.01		. .
S	18.18	. .		18.21

Nonyl Thiophane Sulphone,



For oxidation of the nonyl sulphur compound, the fraction $106^\circ\text{--}108^\circ$ (50 mm.) was selected. In the first half of the oxidation the potassium permanganate was added slowly, in a bath of ice and salt. The reaction was completed at ordinary temperatures, and it proceeded much more slowly toward the end. The required amount of permanganate was consumed in

4 days, and no sulphuric acid was formed. In all these oxidations doubtless sulphonic acids were formed to some extent, but their removal was insured by neutralizing with sodium hydroxide and extraction of the evaporated residue with anhydrous ether. The sp. gr. of the nonyl sulphone was found to be 1.1161, at 20°. Analysis:

I. 0.1867 gram substance gave 0.3874 gram CO_2 and 0.1509 gram H_2O .

II. 0.1679 gram substance gave 0.2071 gram BaSO_4 .

	Calculated for $\text{C}_9\text{H}_{18}\text{SO}_2$.	I.	Found.	II.
C	56.83	56.61		. .
H	9.47	9.04		. .
S	16.84	. .		16.93

Undecyl Thiophane Sulphone,



We were unable to isolate an oxidation product which corresponded closely in composition to decyl thiophane sulphone from the original fraction, and the amount of the thiophane isolated was not sufficient for oxidation.

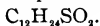
Undecyl thiophane sulphone was prepared from the undecyl thiophane, separated from the fraction 129°-131° (50 mm.); 7.8 grams of the thiophane gave 5 grams of the oxidation product. The heavy oil, left after distillation with steam, had a pleasant, sweetish odor; its sp. gr. was found to be 1.1126, at 20°. Analysis:

I. 0.1903 gram substance gave 0.4176 gram CO_2 and 0.1621 gram H_2O .

II. 0.1470 gram substance gave 0.1579 gram BaSO_4 .

	Calculated for $\text{C}_{11}\text{H}_{22}\text{SO}_2$.	I.	Found.	II.
C	60.54	59.84		. .
H	10.09	9.53		. .
S	14.68	. .		14.75

Dodecyl Thiophane Sulphone,



After treating 7 grams of the distillate 142°-144° (50 mm.)

with 9 grams of potassium permanganate, the proportions found most suitable, there still remained a slight odor of the thiophane, which was completely removed by distillation with steam. The oil that remained after extraction of the steam residue with ether gave, as its sp. gr. at 20° , 1.1372. Analysis :

I. 0.1533 gram substance gave 0.3483 gram CO_2 and 0.1402 gram H_2O .

II. 0.1645 gram substance gave 0.1554 gram BaSO_4 .

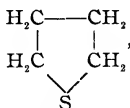
	Calculated for $\text{C}_{12}\text{H}_{24}\text{SO}_2$.	I.	Found.	II.
C	62.07	61.98		. .
H	10.35	10.23		. .
S	13.79	. .		12.91

The sulphur compounds in Canadian petroleum have been shown to belong to a series C_nH_{2n} . Their structure must be explained either as unsaturated, like the ethylene sulphides, or by a ring arrangement. That these bodies are not of the ethylene series is shown by the facts that the ethylene sulphides are solids, and that they absorb bromine without evolution of hydrobromic acid. The petroleum sulphur compounds have a very high specific gravity, and they evolve hydrobromic acid copiously when treated with bromine. They resemble the well-known series of sulphur compounds in forming addition products with mercuric chloride, in the formation of sulphones, the formation of addition products with alkyl iodides and alkaline hydroxides.

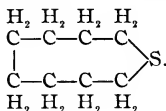
In a former paper by Mabery and Smith it was shown that the sulphur compounds in petroleum are not mercaptans nor thiophens. The series separated by Mabery and Smith from Ohio petroleum formed crystalline addition products with alcoholic mercuric chloride, and the sulphur oils themselves resembled the alkyl sulphides. But the series contained in the portions of Canadian petroleum with higher boiling points are not alkyl sulphides, mercaptans, thiophens, nor ethylene sulphides. Their high specific gravity shows that they belong to a new series. The cyclic condition of the constituents of

Pennsylvania, Ohio, Canadian, Texas and California petroleum corresponding to the series C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , etc., has been described in former papers, and the proportions of these series are indicated by the differences in specific gravity. Canadian petroleum is composed, for the most part, of the series of hydrocarbons poorer in hydrogen. Other constituents of petroleum partake of a similar cyclic condition. The nitrogen compounds, for example, in California petroleum, are tetrahydro and octohydro bodies, with a structure resembling that of the hydroquinolines.

Empirically, the thiophanes are hydrothiophens with long side chains, methylene sulphides with numerous or long side chains, or simple ring methylene sulphides. Either class of formulas will satisfy the results of analysis. For example :

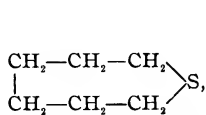


Tetrahydrothiophene or
pentamethylene sulphide.

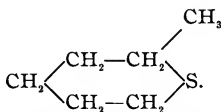


The ready formation of sulphones, addition products with alkyl iodides and hydrates, is unlike the thiophens, but the hydrothiophens may behave differently. It is improbable that rings with a very large number of carbon atoms can exist. A condensed ring structure like quinoline or naphthoquinoline, with sulphur in place of nitrogen, is excluded by the series C_nH_{2n} .

As shown above, the lowest member of the series separated from Canadian petroleum was $C_6H_{12}S$, boiling point $45^\circ-50^\circ$ (50 mm.), which may be hexamethylene sulphide, or methylpentamethylenesulphide. Higher homologues may reasonably be considered as side chain derivatives :



Hexamethylene sulphide.



Methylpentamethylene sulphide.

The structure of these bodies will doubtless have to be referred to the methylene ring, yet the precise form of the ring with reference to the number of carbon atoms it contains is still uncertain. For instance, the central group may be a penta, hexa, or heptamethylene ring. It has, therefore, seemed advisable to employ a comprehensive name that shall include any possible arrangement, and the term thiophane has been adopted. Without doubt, the structure of these sulphur derivatives will be defined with greater precision when the structure of the hydrocarbons of the series C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , etc., which constitute the greater part of the constituents of petroleum with high boiling points from any source, are better understood.

Unsaturated Hydrocarbons of the Series C_nH_{2n} .

The need of more accurate information concerning the presence of hydrocarbons of the ethylene series, C_nH_{2n} , in petroleum, was explained in a former paper of this series. Notwithstanding persistent attempts in the numerous treatises on petroleum to show that these bodies have been identified, a critical examination of published results fails to reveal adequate proof of sufficient foundation for these statements. The statement in "Petroleum and Its Products," by Redwood, that De la Rue and Mueller proved the presence, in preponderating quantities, of the ethylene group in Rangoon petroleum is not supported by the results, nor by the conclusions of those authors. Concerning the results of Warren, Schorlemmer and Chandler, it is not true, as asserted by Redwood, that those chemists found the ethylene series in Pennsylvania petroleum. There are no allusions to this series in Schorlemmer's published papers.

Beyond adopting the general nomenclature then accepted for the ethylene series, Warren evidently left it an open question as to what should be the structural formulæ of the products he separated from Pennsylvania petroleum. There are no statements in his papers to show that he made any further preparation of his products for analysis than boiling with sodium, and no further examination to prove structural forms.

Certainly it would have been easy to demonstrate the unsaturated condition of those bodies had they contained doubly bonded carbon, and in view of Warren's clear-sighted and painstaking methods, he could not have overlooked the importance of those tests. In none of his papers on Pennsylvania petroleum does the term olefine or ethylene appear.

The assertion of Hoefer that members of the olefine series, C_2H_4 to $C_{30}H_{60}$, have been found in American petroleum, has no foundation. In fact, besides the investigations within recent years in this laboratory leading to a better knowledge of the various series of hydrocarbons with high boiling points, no attempts have been made to discover the true composition of American petroleum. In fractions below 200° from Galician oil, Lachowicz obtained no reaction with bromine, yet, so far as they have been examined in this laboratory, distillates below 200° from American oils do not fail to show a considerable bromine absorption. The sulphur compounds in Ohio and Canadian oils have a great affinity for bromine. Substitution may take place in the aromatic hydrocarbons which American oils contain, as well as in the hydrocarbons C_nH_{2n+2} , unless light is excluded. All these bodies, and probably others, are affected in the ordinary determinations of bromine absorption.

At the suggestion of one of us (C. F. M.), in connection with another line of work on petroleum, Mr. T. A. Hicks, a student in this laboratory, undertook a study of bromine absorption in crude oil and in fractions obtained from it after various modes of treatment. Two determinations in the oil before treatment gave, as the percentage of bromine absorbed, (I.) 8.43 and (II.) 8.73. A portion agitated with alcoholic mercuric chloride, washed and dried, gave (I.) 9.27 and (II.) 9.58, indicating that the crude oil holds in solution, to some extent, the mercuric chloride compound. After treatment with mercuric chloride, a portion of the oil shaken with common concentrated sulphuric acid gave with bromine, (I.) 5.91 and (II.) 5.94. The oil was next shaken with fuming sulphuric acid, washed and dried, when it absorbed bromine equivalent to (I.) 3.47 and (II.) 3.72. A portion of the oil, after the last treatment, was distilled under atmospheric pres-

sure, fractions collected at 100° – 125° , 125° – 200° , and 200° – 230° . In the first distillate the bromine absorption was, (I.) 4.65, (II.) 4.75; in the second (I.) 4.63, (II.) 4.58; and in the third (I.) 5.61, (II.) 5.17 per cent. Another portion of the treated oil was distilled under 50 mm., collecting at 130° – 160° , 160° – 190° , 190° – 260° , and a residue, and the bromine absorption determined. Bromine absorption gave in the first distillate (I.) 1.73, (II.) 2.00; in the second (I.) 1.96, (II.) 2.01; in the third (I.) 3.28, (II.) 3.15; and in the residue 9.52. From these results it is evident that substitution in the less volatile portions of the crude oil or cracking has much to do with the amount of bromine absorbed, especially since, in these experiments, the reagents employed for the removal of the sulphur compounds should also remove unsaturated hydrocarbons. In this connection Mr. Hicks determined bromine absorption in some distillates from Pennsylvania, Ohio and Canadian oils, that has been especially purified by long distillation and treatment with reagents, as has been more fully described in another paper. A distillate, 194° – 196° , from Pennsylvania petroleum, gave 0.02 per cent bromine absorbed; another, 209° – 210° , 0.09 per cent; a distillate, 209° – 210° Ohio, purified in the same manner, gave 0.03 per cent bromine, and a Canadian distillate, 0.12 per cent. These results may be accepted as showing no absorption of bromine, since this method is not capable of indicating such small percentages. That the quantity of sulphur remaining in the crude oil, after treating with fuming sulphuric acid, was too small to affect the amount of bromine absorbed, is shown by the low percentage of sulphur, 0.09 and in the distillate 200° – 230° , atmospheric pressure, 0.001 per cent.

When the complex composition of American petroleum is borne in mind, and the probability of substitution in the less volatile portions, the difficulties in testing for unsaturated hydrocarbons are evident. Consequently, all discussion of this subject by those best informed has been undertaken with reservation, while those of others partake more of the nature of speculation on results which the authors were content merely

with presenting, without attempting explanations which the facts were insufficient to justify.

We have had good evidence that unsaturated hydrocarbons are contained in distillates prepared from crude petroleum. Polymerization on standing, the formation of dark colored, heavy oils can only be explained by changes in unsaturated hydrocarbons or unsaturated sulphides. Heptylene was described in another paper as a constituent of Ohio oil.

Since the products described in this paper were contained in the oil extracted with sulphuric acid from burning oil distillate, we have assured ourselves, by experiments already described, that ordinary concentrated sulphuric acid, such as is used in refining burning oil distillates, removes from such distillates, without decomposition, the unsaturated hydrocarbons as well as the sulphur compounds, and, consequently, that the sludge oil, after carefully separating from the acid, contained constituents of the crude oil and not products of decomposition.

In fractioning *in vacuo*, as previously explained, a considerable proportion of the distillates from the sludge oil collected below 100° , which could be distilled without decomposition under atmospheric pressure. These portions were, therefore, carried through 10 distillations under atmospheric pressure, and the portions distilling below 150° *in vacuo* also through 10 additional separations *in vacuo*. On account of great pressure of other work, these distillates stood 3 years before their study was resumed, although, when first obtained, they received sufficient attention to show that they contained unsaturated hydrocarbons.¹

Upon returning to these distillates, it was found that some of them had undergone a marked change. Those collected at certain temperatures—especially at 44° – 45° , seventh distillation (50 mm.); 70° – 71° , twenty-second distillation (atmospheric pressure); 97° – 98° , tenth distillation (atmospheric pressure); 118° – 119° , tenth distillation (atmospheric pressure)—corresponding, in part, to the boiling-points of well-known hydrocarbons of the ethylene series, C_nH_{2n} , had deposited

¹ THIS JOURNAL, 16, 92.

heavy, dark red oils in considerable quantities, evidently products of polymerization. Some of the polymerized oils were found to contain as much as 8 per cent of sulphur, although polymerization took place in oils containing not more than 1.5 per cent of sulphur. It was interesting to observe that distillates on either side of those from which the heavy oils separated remained unchanged and were scarcely more discolored than when they were first distilled. That the distillates below 150° contain sulphur compounds with a peculiar odor, attacking the eyes, and in other respects different from the series $C_nH_{2n}S$ described above, has been apparent since the first distillation of these oils, although these peculiar compounds are evidently present in much smaller proportions than the others.

All these fractions, as well as those above 150° , united with bromine with explosive violence, and with the evolution of great heat. The bromine addition products, however, were found to be so unstable that it was impossible to purify them by distillation even *in vacuo*. They decomposed rapidly, even on standing, with the separation of hydrobromic acid. In ascertaining the composition of these hydrocarbons we have, therefore, relied on the more stable addition product obtained with hydrobromic acid, which had the further advantage that, having no action on the sulphur compounds, the latter need not be removed before heating with the acid.

Hexylene.

For the identification of hexylene, the small quantity of the fractions 70° – 80° , twenty-second distillation (atmospheric pressure), were put together, and a portion was heated to 120° , during 5 hours, with fuming hydrobromic acid. The product was washed, dried and fractionated *in vacuo*. On account of the higher boiling point of the bromide it was easy to separate the addition product and, of the small quantity obtained, the greater portion collected at 62° – 65° (50 mm.). The boiling point of the bromide under atmospheric pressure could not be determined on account of its instability, but it probably was not far from 135° . The distillate selected for the formation of this bromide was nearly the same in boiling point as that of

the hexylenes from various sources, 65° – 70° . Upon analysis values were obtained corresponding to those required for monobromhexane :

I. 0.1938 gram oil gave 0.3108 gram CO_2 and 0.1283 gram H_2O .

II. 0.2720 gram oil gave 0.3045 gram AgBr.

	Calculated for $\text{C}_6\text{H}_{13}\text{Br}$.	I.	Found.	II.
C	43.63	48.73		. .
H	7.88	7.41		. .
Br	48.51	. .		47.64

On account of the small amount of this substance it was not possible to purify it more completely.

Heptylene.

The fractions 98° – 102° , tenth distillation (atmospheric pressure), more nearly corresponding to the boiling points of the various heptylenes, 90° – 100° , were selected especially because they contained a considerable quantity of the polymerized oil. On either side of these limits the distillates had not changed. After treatment with fuming hydrobromic acid and fractioning *in vacuo*, the greater portion of the bromide collected at 76° – 80° (50 mm.). It could not be distilled under atmospheric pressure, but its boiling point was probably not far from 160° . The results of analysis corresponded to the composition of monobromheptane :

I. 0.2000 gram oil gave 0.3498 gram CO_2 and 0.1592 gram H_2O .

II. 0.2117 gram oil gave 0.2188 gram AgBr.

	Calculated for $\text{C}_7\text{H}_{15}\text{Br}$.	I.	Found.	II.
C	46.97	47.71		. .
H	8.38	8.90		. .
Br	44.73	. .		43.99

The sp. gr. of this heptyl bromide was found to be 1.1601.

Octylene.

Octylene was sought for in the fraction 118° – 119° , tenth distillation (atmospheric pressure), from which had separa-

ted a small quantity of the heavy polymerized oil. After heating with concentrated hydrobromic acid, the oil was fractioned *in vacuo* until 15 grams collected at 93° – 95° (50 mm.), corresponding, approximately, to 180° , atmospheric pressure. The boiling point of the distillate selected is near that of diisopropyl ethylene, 116° – 120° , and also that of the octylene, 115° – 117° , prepared from octyl chloride by Schorlemmer.

Analyses of the bromide gave values required for monobrom-octane :

I. 0.1941 gram oil gave 0.3486 gram CO_2 and 0.1613 gram H_2O .

II. 0.1885 gram oil gave 0.1851 gram AgBr.

	Calculated for $\text{C}_8\text{H}_{17}\text{Br}$.	I.	Found.	II.
C	49.74	49.00		. .
H	8.81	9.23		. .
Br	41.45	. .		41.83

The sp. gr. of this octyl bromide was found to be 1.1836.

Nonylene.

The fraction 140° – 141° , tenth distillation (atmospheric pressure) was selected for the addition of hydrobromic acid. In fractioning the bromide *in vacuo*, after the separation of the portion not affected by the acid, the temperature rapidly rose to 110° , and more of the distillate collected at 110° – 113° than at any other point in this vicinity. This product was less stable than the lower homologues, but its boiling point under atmospheric pressure would probably be in the vicinity of 200° . Upon analysis it gave values required for bromnonane :

I. 0.1798 gram oil gave 0.3481 gram CO_2 and 0.1501 gram H_2O .

II. 0.2117 gram oil gave 0.1888 gram AgBr.

	Calculated for $\text{C}_9\text{H}_{19}\text{Br}$.	I.	Found.	II.
C	52.17	52.80		. .
H	9.18	9.33		. .
Br	38.65	. .		37.96

The sp. gr. of this bromnonane was 1.2084.

Higher fractions failed to give us addition products with hydrobromic acid, either because the additive power of the hydrocarbon was too weak, or because, if the addition product were formed, it was decomposed by distillation *in vacuo*. The first explanation is probably correct, since we have never noticed the evolution of hydrobromic acid in any considerable quantity. Perhaps it is more reasonable to assume that our distillates contained no higher homologues of this series than those that were identified.

With reference to the solvent power of sulphuric acid for the hydrocarbons described above, it is doubtless true that compounds with this acid of the hydrocarbons with high molecular weights are less stable, and partake more of the nature of mechanical solution. It is, doubtless, also true that the mechanical solvent power of the acid is increased by the other oils that the acid dissolves. If the acid solution separated from the oil be neutralized with calcium hydroxide, certain lime salts are formed, crystallizing in long needles, and consisting, at least in part, of nitrogen bases, but sulphonates of the ethylene hydrocarbons and of allied series have not been observed. That unsaturated hydrocarbons may be extracted by sulphuric acid and precipitated by dilution, has been shown in several experiments. We diluted a carboy of sludge acid by pouring slowly into water, and found the precipitated oils to contain these hydrocarbons. As to their relative proportion in the crude oil we have no precise data, but in comparison with the principal constituents it is extremely small.

Since the sulphur compounds described in this paper, as well as the alkyl sulphides, are also readily soluble in sulphuric acid, they should be removed as a part of the sludge in refining burning oil distillates.

The results described in this paper may be summarized as follows: The separation from Canadian petroleum of the following series of sulphur compounds: hexyl, heptyl, octyl, nonyl, decyl, undecyl, quatdecyl, sexdecyl, octodecyl thiophanes; the formation of corresponding sulphones by oxidation.

Canadian petroleum contains, in minute proportions, un-

saturated hydrocarbons, C_nH_{2n} , apparently of the ethylene series. Canadian petroleum contains certain sulphur-free oils soluble in alcohol, and different in odor and in other respects from the series hitherto identified in petroleum, possibly terpenes.

We desire to acknowledge our obligations to Messrs. C. A. Lattimer and R. C. McBride for assistance in the purification and analysis of the sulphur compounds.

Contributions from the Sheffield Laboratory of Yale University.

CXXX.—THE RELATIVE SOLUBILITY OF SOME
DIFFICULTLY SOLUBLE CALCIUM AND
BARIUM SALTS.

BY H. W. FOOTE AND G. A. MENGE.

It is well known that the readily soluble salts of calcium are, in general, more soluble than the corresponding barium salts. This is true, for instance, of the chlorides, bromides, iodides, nitrates and chlorates. Of the difficultly soluble salts calcium sulphate is, of course, more soluble than barium sulphate.

In the following investigation the attempt has been made to measure the relative solubility of

- (a) Calcium and barium carbonates,
- (b) Calcium and barium oxalates,
- (c) Calcium and barium fluorides.

By the term "relative solubility" is meant the ratio of the solubility of each salt alone, in water, at a given temperature.

The method which we adopted consisted essentially in treating the difficultly soluble calcium salt with a solution of barium chloride of known concentration and the corresponding barium salt with an equivalent solution of calcium chloride. The mixtures were shaken until no further action occurred, as determined by analysis, and from the proportions of barium and calcium in the solution we hoped to be able to calculate the relative solubilities. This could not be done accurately in every case, as will be shown.

Calcium and Barium Carbonates.

In a saturated solution of calcium carbonate alone, or of barium carbonate alone, the following expressions would hold in case hydrolysis were absent :

$$\text{Ca} \times \text{CO}_3 = K_1 \quad (1) ;$$

$$\text{Ba} \times \text{CO}_3 = K_2 \quad (2).$$

The chemical symbols stand for the concentrations and K_1 and K_2 represent the solubility products¹ of calcium carbonate and barium carbonate, respectively.

Since in (1) $\text{Ca} \equiv \text{CO}_3$ and in (2) $\text{Ba} \equiv \text{CO}_3$, it follows that

$$\text{Ca}^2 = K_1 \quad (3),$$

$$\text{Ba}^2 = K_2 \quad (4),$$

and, as the amounts of calcium and barium are equivalent to calcium carbonate and barium carbonate,

$$\text{Ca} \equiv \text{CaCO}_3 = \sqrt{K_1} \quad (5) ;$$

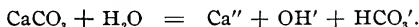
$$\text{Ba} \equiv \text{BaCO}_3 = \sqrt{K_2} \quad (6).$$

Dividing (5) by (6),

$$\frac{\text{CaCO}_3}{\text{BaCO}_3} = \frac{\sqrt{K_1}}{\sqrt{K_2}} \quad (7).$$

That is, excluding hydrolysis, the relative solubility of calcium and barium carbonates is equal to the ratio of the square roots of their solubility products.

A saturated, aqueous solution of calcium or barium carbonate is, however, largely hydrolyzed,²



Letting the chemical symbols represent concentrations, as before,

$$\text{Ca}'' \times \text{OH}' \times \text{HCO}_3' = K_1 \quad (8) ;$$

$$\text{Ba}'' \times \text{OH}' \times \text{HCO}_3' = K_2 \quad (9) ;$$

from which it follows that

¹ Ostwald : "Grundriss der allgem. Chem.," p. 427.

² Küster : Z. anorg. Chem., 22, 161.

$$\frac{\text{CaCO}_3}{\text{BaCO}_3} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} \quad (10).$$

That is, in case of complete hydrolysis, the relative solubility of calcium and barium carbonates is equal to the ratio of the cube roots of their solubility products. As will be seen in Table I., the values calculated from expressions (7) and (10) do not differ very greatly in the case of the carbonates.

In our experiments, calcium carbonate was treated with a solution of barium chloride, and barium carbonate with a solution of calcium chloride :



When equilibrium has taken place, the solution must be saturated in regard to both calcium and barium carbonates, but the amount of calcium and barium ions is vastly in excess of carbonate ions.

In this solution, disregarding hydrolysis,

$$\text{Ca} \times \text{CO}_3 = K_1 \quad (11),$$

$$\text{Ba} \times \text{CO}_3 = K_2 \quad (12),$$

in which K_1 and K_2 represent the same solubility products as in (1) and (2).

The carbonate ions, in their effect on mass action, are common to both the carbonates, so dividing (11) by (12),

$$\frac{\text{Ca}}{\text{Ba}} = \frac{K_1}{K_2} \quad (13).$$

The same expression is obtained when hydrolysis is assumed to take place.

Since calcium and barium salts have about the same tendency to dissociate, in a solution of the two chlorides the ratio of the calcium ions to the total calcium chloride would be nearly the same as the ratio of the barium ions to the total barium chloride and (13) may, therefore, be written

$$\frac{\text{CaCl}_2}{\text{BaCl}_2} = \frac{K_1}{K_2} \quad (14).$$

Combining (7) and (14),

$$\frac{\text{CaCO}_3}{\text{BaCO}_3} = \frac{\sqrt{K_1}}{\sqrt{K_2}} = \sqrt{\frac{\text{CaCl}_2}{\text{BaCl}_2}} \quad (15).$$

That is, the relative solubility of the carbonates is expressed by the square root of the ratio of the calcium and barium chlorides, in case the pure carbonates did not hydrolyze in water.

Combining (10) and (14),

$$\frac{\text{CaCO}_3}{\text{BaCO}_3} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} = \sqrt[3]{\frac{\text{CaCl}_2}{\text{BaCl}_2}} \quad (16),$$

or, the relative solubility of the carbonates is expressed by the cube root of the ratio of calcium and barium chlorides, in case the pure carbonates hydrolyzed completely in water.

The latter assumption of complete hydrolysis is probably more nearly correct, as the carbonates are so insoluble. Kohlrausch and Rose¹ found by determining the electrical conductivity, that a liter of water dissolved about 0.25 mg. equivalents of the carbonates at 18°, so that the saturated solutions would be about 0.00025 N. This value is probably not very exact, as the hydrolysis of the salts appears not to have been taken into account and the results given above are omitted from a table of corrected solubilities given later by Kohlrausch.² The results indicate, however, that the carbonates are very insoluble. The hydrolysis of solutions containing sodium carbonate has been measured by Shields³ at 25°. He obtained the following results:

Na ₂ CO ₃ (gram-mols. per liter).	Per cent of hydrolysis.
0.19	2.12
0.094	3.17
0.0477	4.87
0.0238	7.10

While accurate extrapolation for very dilute solutions is impossible from these results, they serve to show that a solution of sodium carbonate as dilute as a saturated solution of calcium carbonate, would be largely hydrolyzed. Calcium car-

¹ Z. physik. Chem., 12, 234.

² *Ibid.*, 50, 355.

³ *Ibid.*, 12, 167.

bonate should hydrolyze to about the extent that sodium carbonate does, as the acid radical is the same and the hydroxides of calcium and sodium are both strong bases. The relative solubility of calcium and barium carbonates would, therefore, be represented more accurately by expression (16) $\sqrt[3]{\frac{\text{CaCl}_2}{\text{BaCl}_2}}$

than by (15) $\sqrt{\frac{\text{CaCl}_2}{\text{BaCl}_2}}$.

For the experiments pure calcium and barium carbonates were prepared by precipitating solutions of the chlorides with ammonium carbonate, in excess. Barium carbonate was precipitated from a hot solution. Calcium carbonate was precipitated cold and the precipitate and solution heated to boiling. In this way the salt was obtained in minute calcite crystals, which are more stable than the aragonite obtained by precipitating from a hot solution.¹ The carbonates were thoroughly washed and dried.

Solutions of calcium and barium chlorides, 0.1 N, were prepared and accurately standardized, and from these 0.05 N solutions were made by diluting.

In analyzing solutions containing both calcium and barium chlorides in contact with the carbonates, 25 cc. of solution were drawn off with a pipette through a plug of glass wool. The solution was diluted, acidified with a very few cc. of acetic acid, heated and about 10 cc. of a 10 per cent solution of ammonium chromate added. The latter was prepared from ammonium bichromate, by adding a calculated amount of ammonium hydroxide, not quite sufficient to form the normal salt. The barium chromate formed was allowed to stand, then filtered on a Gooch crucible, ignited and weighed. Calcium could be determined in the filtrate as oxalate, but this was not necessary with the carbonates, as the amount present in a given volume could be calculated when the barium was known. It was necessary to determine both calcium and barium when working with the oxalates and fluorides, on account of their greater solubility.

¹ Z. physik. Chem., **33**, 740.

Test analyses on known amounts of barium in the presence of calcium gave excellent results by the method described above.

A preliminary experiment was tried by treating a large excess of calcium carbonate, in a bottle, with a solution of barium chloride, approximately 0.1 N, and in another bottle an excess of barium carbonate with a similar solution of calcium chloride. A small amount of the other carbonate was added in each case. The bottles were shaken for several weeks on a revolving shaft, at room temperature. The following results were obtained :

	Carbonates used.		Initial solution, milligram equivalents per liter.		Final solutions, milligram equivalents per liter.	
	CaCO ₃ . Gram.	BaCO ₃ . Gram.	Ca.	Ba.	Ca.	Ba.
I.	45	0.2±	0.00	100	52	48
II.	0.2±	45	100	0.00	72	28

The final solutions obtained, which should have been alike if equilibrium had been reached, were still very far removed from each other and showed that equilibrium could be reached in this way only very slowly. The experiment showed, however, that for equilibrium the ratio $\frac{\text{Ca}}{\text{Ba}}$ would lie between $\frac{52}{48}$

and $\frac{72}{28}$. As this experiment had proceeded so slowly, it was evident that very thorough shaking was necessary to make the carbonates react with the chlorides.

We, therefore, did not carry on the experiment in a thermostat, but the bottles containing the mixtures were placed, as before, on a revolving shaft which was running throughout the day, the temperature varying between 15° and 21°. Glass beads or garnets were put in the bottles to keep the precipitate suspended. Without the beads the precipitate tended to harden on the sides of the bottle, due to centrifugal action.

From 200 to 300 cc. of liquid were placed in the bottles with an excess of the carbonates. Instead of starting with pure calcium chloride or barium chloride solutions, the equivalent solutions of these two salts were mixed together in known pro-

portions, so that the ratio $\frac{\text{Ca}}{\text{Ba}}$ at the beginning was between $\frac{58}{42}$ and $\frac{72}{28}$, the preliminary experiment having shown that final equilibrium would lie between these extremes. In this way much time could be saved in shaking. An excess of each carbonate was used, so that the reaction could proceed in either direction. The mixtures were shaken several weeks. Samples were drawn off at intervals and barium determined till there was no further action apparent. In this manner the results given in Table I. were obtained.

In the last two columns the ratios $\sqrt{\frac{\text{Ca}}{\text{Ba}}}$ and $\sqrt[3]{\frac{\text{Ca}}{\text{Ba}}}$ have been calculated from the final solutions obtained and these results are nearly constant. The values do not differ much from each other, but the second expression is probably more nearly correct, so that

$$\text{Relative solubility, } \frac{\text{CaCO}_3}{\text{BaCO}_3} = 1.20.$$

In the preceding work we have assumed that the carbonates of barium and calcium do not form mixed crystals. In that case only would the solubility relations derived above hold strictly. That each carbonate cannot form an unlimited series of mixed crystals with the other is shown by the fact that the stable crystal form of each is different, calcium carbonate is rhombohedral and barium carbonate orthorhombic. It was probable, however, that the two carbonates could form a limited series of mixed crystals in which each would dissolve a limited amount of the other carbonate. Such mixed carbonates of calcium and barium occur in nature. Should such mixed crystals be produced, the carbonates present in the experiments of Table I. would not be a mechanical mixture of the two pure carbonates, but a mixture of the two carbonates, each saturated with the other, and the relative solubility previously determined would be the relative solubility of these two kinds of mixed crystals. In general, the solubility of a

Table I.
0.1 N CaCl_2 and BaCl_2 .

No.	CaCO_3 , Grams.	BaCO_3 , Grams.	Initial solutions, milligram equivalents per liter.		Final solutions, milligram equivalents per liter.		$\sqrt{\frac{\text{Ca}}{\text{Ba}}}$.	$\sqrt[3]{\frac{\text{Ca}}{\text{Ba}}}$.
			Ca.	Ba.	Ca.	Ba.		
1	40	40	56.83	43.17	63.30	36.70	1.31	1.20
2	40	40	62.01	37.99	63.30	36.70	1.31	1.20
3	40	40	67.15	32.85	62.37	37.27	1.30	1.19
0.05 N CaCl_2 and BaCl_2 .								
4	20	20	31.16	18.84	31.42	18.58	1.30	1.19
5	20	20	33.50	16.50	32.08	17.92	1.34	1.21

Table II.

0.05 N CaCl_2 and BaCl_2 .

No.	CaCO_3 , (Grams.)	BaCO_3 , (Grams.)	Initial solution, milligram equivalents per liter.		Final solution, milligram equivalents per liter.		$\sqrt[3]{\frac{\text{Ca}}{\text{Ba}}}$.
			Ca.	Ba.	Ca.	Ba.	
1	50	0.1 \pm	31.75	18.25	31.89	18.11	1.21
2	0.1 \pm	43.0	31.75	18.25	28.02	21.98	1.08

salt diminishes as the amount of salt with which it forms a mixed crystal increases.¹

To determine whether or not mixed crystals were formed in the preceding experiments we proceeded in the following manner: A 0.05 N solution of the two chlorides was prepared, in which the salts were present in the proportion required for equilibrium as shown in Table I., Nos. 4 and 5. Part of this solution was treated with barium carbonate, containing a minute amount of calcium carbonate to induce crystallization, and the other part was treated with calcium carbonate containing a very small amount of barium carbonate. In each experiment, then, one carbonate or the other was present in practically pure condition. These mixtures were shaken as before for 2 weeks and the solutions analyzed. In case mixed crystals of the two carbonates had not formed in the previous work, there would be the same solid phases here as before, in Table I., and we should expect no change in the solution. If mixed crystals had formed before, the pure carbonate in excess, in the present experiments, would tend to have a greater relative solubility than indicated in Table I. and the relation of calcium and barium chlorides in solution would change accordingly. The results recorded in Table II. were obtained.

The solution in the first experiment remained practically constant and the same as the final solutions in Table I., showing that calcium carbonate had not taken up an appreciable amount of barium carbonate in the experiments given in Table I. In the second experiment (Table II.) the barium in solution increased and the calcium decreased. As the barium carbonate in this case was practically pure, this result indicates that the barium carbonate in the experiments of Table I. must have taken up a certain amount of calcium carbonate to form mixed crystals.

Summarizing the results in Table II.,

$$\text{Relative solubility } \frac{\text{CaCO}_3}{\text{BaCO}_3 \text{ saturated with CaCO}_3} = 1.21,$$

$$\frac{\text{CaCO}_3 \text{ dissolved in BaCO}_3}{\text{BaCO}_3} = 1.08.$$

¹ Roozeboom : Z. physik. Chem., 10, 145.

The average of these values should represent very nearly the relative solubility of the two pure carbonates, or

$$\text{Relative solubility } \frac{\text{CaCO}_3}{\text{BaCO}_3} = 1.15.$$

This result, allowing for mixed crystals, differs but little from the one in which no allowance was made.

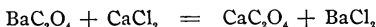
Calcium and Barium Oxalates.

As oxalic acid is a comparatively strong acid, the hydrolysis of the oxalates with water can be neglected, and an expression similar to that for the carbonates, when hydrolysis is assumed to be absent, can be used to represent the relative solubility of barium and calcium oxalates :

$$\frac{\text{CaC}_2\text{O}_4}{\text{BaC}_2\text{O}_4} = \frac{\sqrt{K_1}}{\sqrt{K_2}} = \sqrt{\frac{\text{CaCl}_2}{\text{BaCl}_2}}.$$

K_1 and K_2 represent the solubility products of the respective oxalates.

It was found that barium oxalate is much more readily soluble than calcium oxalate so that the reaction



is very nearly complete. In fact, barium oxalate has an appreciable absolute solubility, and it was necessary to determine the amount of both calcium and barium in solution, although solutions of known concentration of the chlorides were used as before.

The oxalates were prepared by precipitating the chlorides from a hot solution with ammonium oxalate, in excess. They were thoroughly washed and dried. Solutions of barium and calcium chlorides, 0.1 N and 0.05 N, were used, as before.

The results obtained are given in Table III. The first two experiments were preliminary and only barium was determined directly. In the others, both barium and calcium were determined. Experiments 3 to 6 were shaken about 3 weeks.

Table III.

0.1 N CaCl_2 and BaCl_2 .

No.	CaC_2O_4 (Grams.)	BaC_2O_4 (Grams.)	Initial solution, milligram equivalents per liter.		Final solution, milligram equivalents per liter.		$\sqrt{\frac{\text{Ca}}{\text{Ba}}}$.
			Ca.	Ba.	Ca.	Ba.	
1	15.00 g.	0.2 \pm g.	00.00	100	.	97.35	
2	0.2 \pm	20.00	100.0	00.00	.	95.84	
3	15.0	0.2	3.41	96.59	3.43	100.8	0.18
4	0.2	15.0	3.41	96.59	2.48	98.87	0.16
0.05 N CaCl_2 and BaCl_2 .							
5	15.0	0.2 \pm	00.0	50.0	4.00	47.83	0.29
6	0.2 \pm	20.0	50.0	00.0	2.86	50.35	0.23

The agreement between the 0.1 N and 0.05 N solutions is not very satisfactory, but is largely due to the fact that the amounts of calcium in solution were small, and small errors in determination would give relatively large errors in the ratio. It will be observed that, in the last 4 experiments, the final equilibrium appears not to be independent of the quantities of barium and calcium oxalates. With an excess of calcium oxalate the ratio $\frac{\text{Ca}}{\text{Ba}}$ is greater than with an excess of barium oxalate. Apparently mixed crystals form to a certain extent, which would account for this, but the error from this cause is not greater than the other errors of the experiment.

Taking the average of the 4 results,

$$\text{Relative solubility } \frac{\text{CaC}_2\text{O}_4}{\text{BaC}_2\text{O}_4} = 0.22.$$

Calcium and Barium Fluorides.

The attempt was made to measure the relative solubility of calcium and barium fluorides, but the results are only of qualitative interest.

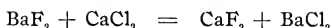
Barium fluoride was made by nearly neutralizing pure hydrofluoric acid with potassium carbonate and treating this solution with a dilute solution of barium chloride, which was not quite sufficient to precipitate all the fluoride. Care was taken that the barium chloride was not added in excess, as a double barium chloride and fluoride apparently precipitated under these conditions. The precipitated barium fluoride was thoroughly washed and dried.

The calcium fluoride used was pure fluor spar, very finely ground.

As these fluorides form three ions in dilute solution, the relative solubility would be represented by an expression similar to that for the hydrolyzed carbonates.

$$\frac{\text{CaF}_2}{\text{BaF}_2} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} = \sqrt[3]{\frac{\text{CaCl}_2}{\text{BaCl}_2}}.$$

On treating barium fluoride with calcium chloride it was found that the reaction



was nearly complete, and the amount of calcium left in solution was too small to determine accurately. Barium fluoride is, therefore, very much more soluble than calcium fluoride, but the relation $\sqrt[3]{\frac{\text{CaCl}_2}{\text{BaCl}_2}}$ is so much affected by slight errors in determining calcium, that reliable quantitative results on the relative solubility of the two fluorides cannot be obtained.

Only 0.05 N solutions of calcium and barium chlorides could be used. A 0.1 N solution reacted with barium fluoride and formed a double fluoride and chloride, removing barium chloride from solution. The results obtained were as follows:

Table IV.

0.05 N CaCl_2 and BaCl_2 .

No.	CaF_2 . (Grams.)	BaF_2 . (Grams.)	Initial solution, milligram equivalents per liter.		Final solution, milligram equivalents per liter.	
			Ca.	Ba.	Ca.	Ba.
1	15.0	0.5±	0.0	50.0	1.36	61.72
2	0.5±	15.0	50.0	0.0	2.00	61.60

The absolute solubility of the carbonates and oxalates of calcium and barium has been determined by Kohlrausch and Rose and by Kohlrausch,¹ by means of the electrical conductivity of the saturated solutions, and the relative solubilities can be calculated from their results and compared with ours. They worked at 18°.

	Solubility, milligram equivalent per liter.	$\frac{\text{Ca}}{\text{Ba}}$. (Kohlrausch.)	$\frac{\text{Ca}}{\text{Ba}}$. (Foote and Menge.)
CaCO_3	0.26 }	1.08	1.15
BaCO_3	0.24 }		
CaC_2O_4	0.087 }	0.11	0.22
BaC_2O_4	0.76 }		

Considering that the results are obtained by two totally different methods, the agreement is as close as could be expected. The method which we have used we believe gives closer results than the conductivity method for the carbonates where

¹ Z. physik. Chem., 12, 234; 50, 355.

the ratio is not far from 1, for slight errors in determining the amounts of calcium and barium in solution would not materially affect the ratio. On the other hand, in the case of the oxalates, the Kohlrausch method should give fully as good results, for by our method a slight error in determining the quantity of calcium, which is present in solution in small amounts, affects the ratio considerably.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
February, 1906.

THE BEARING OF HYDRATES ON THE TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF AQUEOUS SOLUTIONS.

[SIXTEENTH COMMUNICATION.]

BY HARRY C. JONES.

That the electrical conductivity of aqueous solutions of electrolytes, in general, increases greatly with rise in temperature is a well known fact. This might be due either to an increase in the dissociation of the electrolyte with rise in temperature, or to an increase in the velocity with which the ions move, or to both. It is not a difficult matter to test the effect of change in temperature on the dissociation of electrolytes. It is only necessary to measure the dissociation directly, at different temperatures, by the conductivity method. This has been done recently by Jones and West,¹ for temperatures ranging from 0° to 35°. The result is that electrolytes, in general, are *slightly less* dissociated at the higher than at the lower temperatures.

As has been pointed out, this is in accord with the theory of Dutoit and Aston, which makes the dissociating power of a solvent a function of its own association—the more associated a solvent the greater its dissociating power. Take a solvent like water, the higher the temperature the less it is associated and, consequently, the smaller its power to break molecules of electrolytes down into ions.

Having eliminated the factor of dissociation as increasing the conductivity of electrolytes at the higher temperature, we are

¹ THIS JOURNAL, 34, 357 (1905).

forced to conclude that the increase in conductivity with rise in temperature, shown by solutions of electrolytes in general, is due to an increase in the velocities with which the ions move.

There are a number of factors which determine the velocity with which an ion moves through a solution of an electrolyte. Assuming that the force which drives the ions is constant, *the velocity would be conditioned chiefly by the viscosity of the medium through which the ion passed, and by the size of the ion.* At the more elevated temperature the force which drives the ion would be greater, and the viscosity of the medium through which the ion moves would be less. Both of these factors would increase the velocity with which the ions move and, consequently, increase the conductivity as the temperature was raised.

The object of this paper is to call attention to another factor which causes the ions to move faster at the more elevated temperature. *The mass of the ion decreases with rise in temperature.* This does not refer to the charged atom or group of atoms which we usually term the ion, but to this charged nucleus plus a larger or smaller number of molecules of water, which are attached to it, and which it must drag along with it in its motion through the remainder of the solvent.

That ions are hydrated has been shown beyond question by Jones and his co-workers. That these hydrates are relatively unstable compounds has also been demonstrated; the higher the temperature the less complex the hydrates existing in the solution. This can be seen from one example. In a solution of a certain definite concentration, every molecule of calcium chloride, or the ions resulting from it, holds about 30 molecules of water. From such a solution practically all of the water can be removed by simply boiling it, except 6 molecules of water to 1 of calcium chloride—this number being brought out of the solution by the salt as water of crystallization. The higher the temperature, then, the less complex the hydrate formed by the ion. The less the number of molecules of water combined with the ion the smaller the mass of the ion, and the less its resistance when moving through the solvent.

Consequently, the ion will move faster at the high temperature. This conclusion can be tested by the results of experiment. If this factor of diminishing complexity of the hydrate formed by the ion with rise in temperature, plays any prominent rôle in determining the large temperature coefficient of conductivity, then we should expect to find *those ions with the largest hydrating power, having the largest temperature coefficients of conductivity*. This will readily be seen to be the case. The more complex the hydrate, *i. e.*, the greater the number of molecules of water combined with an ion, the greater the *change* in the complexity of the hydrate with rise in temperature. We can readily test this conclusion by the results of the experimental work of Jones and West.¹ Let us compare the temperature coefficients of conductivity per degree rise in temperature, for some of those substances which have slight hydrating power, with the corresponding coefficients for a few of the substances which have a much greater power to combine with water.

The volumes for which the comparisons are made range from 2 to 1024, and the temperatures from 25° to 35°.

A comparison of Table I. and Table II. will show that the above conclusion is confirmed by the experimental results. The substances included in Table I. have very slight hydrating power. Those in Table II. have very much greater hydrating power. It will be remembered that hydrating power is a function of water of crystallization—the larger the number of molecules of water of crystallization the greater, in general, is the hydrating power of the substance. It will be seen that the substances in Table I. have little or no water of crystallization, while those in Table II. crystallize with large amounts of water. The water of crystallization may be taken as roughly proportional to the hydrating power of the substance.

The substances in Table I. have much smaller coefficients of conductivity than those in Table II., even taking into account the fact that those in Table II. are ternary electrolytes, while those in Table I. are binary electrolytes.

¹ THIS JOURNAL, 34, 357 (1905).

Table I.—Substances with Slight Hydrating Power.

	Temperature coefficients in conductivity units.	
	$v = 2.$	$v = 1024.$
Ammonium chloride	2.07	2.94
“ bromide	2.16	2.86
Potassium chloride	2.13	2.84
“ bromide	2.18	2.91
“ iodide	2.09	2.91
“ nitrate	1.86	2.71

Table II.—Substances with Large Hydrating Power.

	Temperature coefficients in conductivity units.	
	$v = 2.$	$v = 1024.$
Calcium chloride	3.11	5.61
“ bromide	3.01	5.20
Strontium “	2.93	5.27
Barium chloride	2.86	5.30
Magnesium chloride	2.55	4.59
Manganese “	2.37	4.86
“ nitrate	2.24	4.16
Cobalt chloride	2.54	4.95
“ nitrate	2.48	4.67
Nickel chloride	2.63	5.04
“ nitrate	2.51	4.58
Copper chloride	2.15	5.04
“ nitrate	2.38	4.88

Another fact, of equal importance, is brought out by comparing the results in Table I. with one another, and similarly those in Table II. with one another. If the temperature coefficient of conductivity is a function of the decrease in the complexity of the hydrate formed by the ion, with rise in temperature, then we should expect that *those substances which have equal hydrating power would have approximately the same temperature coefficients of conductivity.*

If we examine the above tables we shall see that this is true. The substances in Table I. all have only very slight hydrating power, as would be expected from the fact that they all crystallize without water. Their temperature coefficients of conductivity are all of the same order of magnitude and, indeed, are very nearly equal.

The substances in Table II. all have very great hydrating power, and all have a hydrating power of the same order of

magnitude. This would be expected, since nearly all of these substances crystallize with 6 molecules of water. There are a few compounds in this table calling for special comment. Barium chloride crystallizes with only 2 molecules of water, yet it forms hydrates comparable with those substances with larger amounts of water of crystallization. It is, therefore, perfectly in keeping with the above relation that its temperature coefficients of conductivity should be of the order of magnitude that they are in the above table.

Manganese chloride crystallizes with only 4 molecules of water, but the work of Jones and Bassett¹ shows that it forms hydrates about as complex as the other salts in Table II. Its temperature coefficients of conductivity are of the same order of magnitude as the other substances in this table.

Of the compounds recorded in Table II., the one which, apparently, presents the most pronounced exception to the relation that we are now considering, is copper chloride. This salt crystallizes with only 2 molecules of water, and yet has a temperature coefficient of conductivity that is nearly as large as the salts with 6 molecules of water of crystallization. It might be inferred that this salt has much less hydrating power than the others in Table II. The work of Jones and Bassett² shows that this is not the case. Copper chloride has a large hydrating power, indeed much larger than would be expected from the amount of water with which it crystallizes. Its temperature coefficient of conductivity is, therefore, not surprisingly great.

A third point that is brought out by the results in the above tables, is the following: *At the higher dilution the temperature coefficient of conductivity for any given substance is greater than at the lower dilution.* That this is a general relation will be seen by reference to the work of Jones and West.³ This is explained very satisfactorily on the basis of the suggestion made in this paper. The complexity of the hydrate at the higher dilution is greater than at the lower dilution, as is shown by the experi-

¹ THIS JOURNAL, 33, 562 (1905).

² *Ibid.*, 33, 577 (1905).

³ *Ibid.*, 34, 357 (1905).

ments of Jones and his co-workers¹ on the composition of the hydrates formed by different substances at different dilutions.

The hydrate being more complex at the higher dilution, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

The three points that are established in this paper are :

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those substances having, approximately, the same hydrating power.

5. The temperature coefficients of conductivity, for any given substance, increase with the dilution of the solution, and this increase is greatest for those substances with large hydrating power.

All three of these conclusions are necessary consequences of the assumption that the *large change in conductivity with change in temperature is due, in part, to the decreasing complexity of the hydrates formed around the ions*, with rise in temperature. Since these conclusions are all verified by the results of experiment, we must accept the assumption which led to them as containing a large element of truth.

It is more than probable that the decreasing complexity of the hydrates, with rise in temperature, is a very important factor in conditioning the large temperature coefficients of conductivity, especially of those substances which have large hydrating power.

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¹ THIS JOURNAL, 33, 534 (1905) ; 34, 290 (1905).

AN ELECTRICAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF HYDROGEN, CARBON AND SULPHUR IN ORGANIC COMPOUNDS.

BY H. N. MORSE AND C. W. GRAY.

In No. 8, Vol. I., 1906, page 699 of the *Chemischer Central-Blatt*, which has just come into our hands, we find an account of a "New Method for the Analysis of Organic Compounds," by Oreste Carrasco. The original description appeared in *Atti R. Accad. dei Lincei Roma* [5], 14, II., 613, December 3, 1905. It is stated, however, by the one making the abstract for the *Central-Blatt*, that an account of the method was deposited July 30, 1904, in the form of a "sealed communication," which was opened for the first time at the meeting of November 19, 1905.

The method in question is quite similar to one which was described in this JOURNAL, Vol. 33, No. 6, which appeared June 1, 1905, by H. N. Morse and L. S. Taylor, under the title, "An Electrical Method for the Combustion of Organic Compounds." The account of the method of Morse and Taylor was delivered by them in manuscript to the editor of the JOURNAL on March 1, 1905, as appears at the close of the published article, and at that time the method had been fully developed, as is attested by the introductory statements of its authors, as follows: "The process for the Analysis of Organic compounds which is here described has been in general use in this laboratory during the past year and with such satisfactory results that it has almost wholly supplanted the older method of burning organic compounds." In other words, the process in question came into general use in this laboratory early in the year 1904, as early, in fact, as March 1 of that year. Its feasibility must, of course, have been demonstrated at a still earlier date. The idea of the method originated in connection with some work of one of the authors with J. C. Frazer upon "A New Electric Furnace and Various Other Heating Appliances for Laboratory Use," an account of which

was published in this JOURNAL, **32**, 93, and the first experiments with the process were made by him during the year 1903. To sum up the facts having a bearing on the question of priority, it appears :

1. That the method of Morse and Taylor was published on June 1, 1905, and that of Carrasco on December 3, 1905.

2. That the former process had been developed and was in use in this laboratory as early as March 1, 1904, while an account of the latter process—obviously still in an incomplete state—was deposited in the form of a "sealed communication" on July 30, 1904, which was opened for the first time on November 19, 1905.

We now proceed to describe an extension of the method of Morse and Taylor to the simultaneous determination of carbon, hydrogen and sulphur.

The apparatus which is employed is represented in Figs. I. and II. It is identical with that described by Morse and Taylor,¹ except in so far as modifications were made necessary for the purpose of determining sulphur at the same time with carbon and hydrogen. It consists of a thin, hard glass tube open at both ends and having a length of about 600 mm. and an internal diameter of about 20 mm. One end is closed with a rubber stopper through which pass (I.) the small porcelain tube E, having a length of 300 mm. and an external diameter of 6 mm. and (II.) the exit tube L. The T-tube D is slipped over the end of the porcelain tube and is fastened to the latter by means of a short piece of rubber tubing. The horizontal end of D is closed with a stopper through which passes a platinum wire. The wire extends through the whole length of the porcelain tube and returns upon the outside in a series of suspended loops, and then passes out through the rubber stopper, as shown in the figure. The ends of the wire are much thicker than the intermediate portion, in order to avoid the danger of burning the stoppers. To this point the new apparatus is identical with the older one. The first modification which was introduced to adapt the method to the determination of sulphur was to wind the coils in the vicinity of G

¹ THIS JOURNAL, **33**, 591.

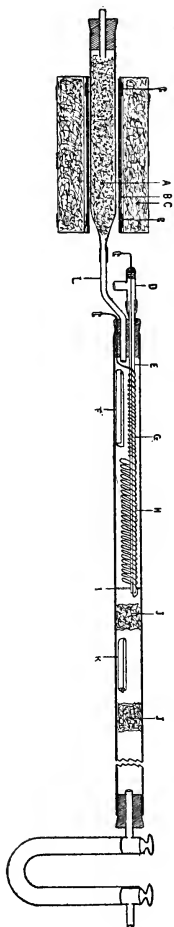


Fig. I.

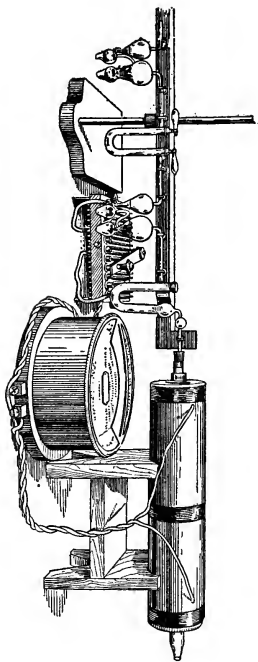


Fig. II.

tightly about the porcelain tube, in order to make room for the long platinum boat F, which, when an analysis is to be made, contains a weighed quantity of pure peroxide of lead. The rear end of the boat is open to facilitate contact between the products of combustion and the oxide. The second change was to remove the rolls of oxidized copper wire gauze which formerly preceded and followed the boat K, and to substitute in their places the asbestos plugs J and J. The rear end of the porcelain tube passes through the eccentrically perforated platinum disk I, and is thereby maintained in its proper position in the glass tube.

The apparatus A B C, in front of the combustion tube, is one designed to complete the absorption of oxides of nitrogen, a portion of which is also retained by the peroxide in F. It consists of the graphited porcelain tube B, which has a length of about 300 mm. and is electrically heated, the asbestos covering C and the glass tube A, which is filled with asbestos covered with peroxide of lead. The tube A is connected on the one side with the combustion tube and on the other with the usual absorption apparatus for water and carbon dioxide.

The method of graphiting porcelain tubes, like B, and other objects for the purpose of electrical heating, has been described by Morse and Frazer,¹ and the procedure need not, therefore, be explained in this connection. To prepare the tube A, asbestos is covered, by sprinkling and mixing, with as much peroxide of lead (which has previously been heated to nearly 300°, *i. e.*, to the temperature necessary for complete dehydration) as can be made to adhere to it; and, after filling the tube, an additional quantity of the peroxide is sifted in among the asbestos fibers. A single filling suffices for a very large number of analyses. During a combustion it is necessary to maintain in the tube A a temperature of about 175°, in order to insure the complete absorption of nitric oxide. The apparatus must, therefore, be subjected to a species of calibration before it is used. To this end a current of dried air, approximately equal to that of the gas which normally flows through an apparatus during a combustion, is passed through

¹ THIS JOURNAL, 32, 93.

A. A thermometer is inserted and the amount of current necessary to maintain a series of temperatures in the tube, *e. g.*, 100° , 125° , 150° , 175° and 200° , is ascertained. Furthermore, the length of time required by a given current to bring the contents of the tube to a constant temperature is determined. A calibration of this kind is not precise, since the rate of flow of gas during a combustion is irregular and at all times of somewhat uncertain magnitude, but it is sufficiently accurate for all practical purposes.

The peroxide of lead which is employed in F for the absorption of the oxides of sulphur is prepared by the method of Dennstedt in the highest practicable state of purity, and is subsequently heated to 300° to insure complete dehydration. The quantity of PbO which a unit weight of it will yield is determined with care, once for all, by heating weighed quantities of the peroxide to constant weight in a current of nitrogen, and the result is employed in finding the amount of sulphur trioxide produced in the combustion. It is necessary, of course, that the peroxide, when weighed, shall be entirely free from moisture; we therefore proceed in the following manner: The boat F, after introducing the requisite amount of the peroxide—about 5 grams—is placed in a horizontal position in a glass weighing tube having a ground glass stopper, the material, boat and tube are then heated for half an hour at a temperature of 120° , and afterwards cooled in a desiccator. When the desiccator is opened for the purpose of weighing, the tube is immediately closed with the stopper.

The procedure, when an analysis is to be made, is as follows: The boat containing the weighed quantity of peroxide is inserted at F, and that containing the substance to be burned at K. The two circuits—that through the combustion apparatus and also that through A B C—are closed through regulating rheostats, and dry air is passed through the whole apparatus—except, of course, the absorption train. The current through A B C is allowed to rise quickly to the quantity which is known to produce in A the most effective temperature for the absorption of nitric oxide—about 175° —while the current through the combustion apparatus is regulated more cautiously,

especially if there is danger of indirectly heating the substance in K to a temperature at which it becomes volatile. Having dried out the whole apparatus, the absorption train is joined to A, the current of dried and purified air entering at the rear is continued, oxygen is admitted at D, and the substance in K—also the plug of asbestos J in front of the boat—is heated by a lamp held in the hand. The flow of oxygen and of air, and the heating of the substance with the lamp, likewise the temperature of the platinum coils, are, thereafter regulated according to the best judgment of the operator. If the substance is so volatile that an explosion is likely to occur between the asbestos plugs, the air admitted at the rear is deprived of its oxygen by inserting a roll of copper wire gauze behind the last asbestos plug and heating it with a lamp appropriately placed under the tube, or nitrogen, instead of air, is passed in from a gasometer.

The platinum coils are maintained at a moderately bright red heat during a combustion. This insures a sufficiently high temperature of the peroxide under the small coils at G, and is ample for the combustion of the vapors of the substance.

The precautions which are taken to prevent the cracking of the glass combustion tube, especially during the cooling-down period, have been sufficiently described in a previous paper,¹ and only one of these will be recalled here—that of blackening the whole of the exposed portion of the tube with a smoky flame as soon as the combustion is finished, and before reducing the current flowing through the platinum wire.

The material in the boat consists, after a combustion, of a mixture of lead peroxide, lead sulphate, and—if the substance contained nitrogen—a small quantity of lead nitrate; and the amount of PbO—supposing all of the lead to be in that state—is known. To find the amount of sulphur, reckoned as SO₃, it is, therefore, only necessary to reduce the peroxide and nitrate in the mixture to oxide and weigh the residue. This reduction is effected in the following manner: The boat, with its contents, is placed in a hard glass tube, and behind it is inserted a roll of copper wire gauze. Both the boat and the roll

¹ THIS JOURNAL, 33, 591.

are heated by lamps and air is passed through the tube ; or the reduction is effected in a current of nitrogen flowing from a gasometer. The decomposition of the nitrate is made manifest by the appearance and subsequent disappearance of reddish vapors, and the reduction of the peroxide by the disappearance of brown and red colors in the material ; nevertheless, the residue is reheated, after weighing, in an atmosphere of nitrogen to ascertain if the weight remains constant.

We give below the results obtained by the analysis of a few substances :

" Sulphonal," $(CH_3)_2C(SO_2C_2H_5)_2$.

	C.	H.	S.
Theoretical	36.80	7.06	28.09
Found	36.69	7.26	28.16
"	36.47	7.12	27.90
"	36.73	7.19	28.03

Phenylthiourea, $NH_2CSNHC_6H_5$.

	C.	H.	S.
Theoretical	55.19	5.29	18.44
Found	55.40	5.24	18.30
"	55.24	5.50	18.53

Phenylthiosemicarbazide, $C_6H_5NHNHCSNH_2$.

	C.	H.	S.
Theoretical	50.22	5.12	19.17
Found	50.38	5.40	18.91
"	50.39	5.50	19.31

Parasulphaminebenzoic Acid, $C_6H_4(SO_2NH_2)COOH$.

	C.	H.	S.
Theoretical	41.76	3.50	15.93
Found	41.84	3.70	16.05
"	41.79	3.57	16.10

In the original form of the method as described by Morse and Taylor¹ for the determination of carbon and hydrogen only, the oxides of nitrogen were reduced by means of metallic copper, and such a reduction, in skilled hands, is practicable and gives satisfactory results, but further experience has shown that this procedure is apt to fail in the hands of be-

¹ THIS JOURNAL, 33, 591.

ginners. In the later practice, therefore, the use of copper has been abandoned, and the oxides of nitrogen are now absorbed by the peroxide of lead in exactly the manner described above. If carbon and hydrogen are to be determined in a compound containing nitrogen but no sulphur, the boat of peroxide at F may be dispensed with and the contents of A relied upon to absorb all the oxides of nitrogen. It is well, however, in burning substances which do not contain sulphur, to replace the plugs of asbestos J J by oxidized rolls of copper wire gauze.

It is stated by Carrasco that his method, in the form described in the "sealed communication"—that is, without any provision for the removal of oxides of nitrogen, "is adapted to substances containing ammoniacal nitrogen, while in the presence of NO_2 groups too high values for carbon are obtained," etc. The first part of the above statement, which is quoted from the abstract in the *Central-Blatt*, is surprising in view of the fact that probably all organic substances containing "ammoniacal" nitrogen yield nitric oxide when burned in oxygen, and many of them notable quantities of it. It would seem that even a little actual experience with his proposed method, as applied to nitrogenous substances, should have convinced its author that, when any compound containing nitrogen, whatever its class, is burned for the purpose of determining carbon and hydrogen, it is wise to make ample provision for the reduction or absorption of oxides of nitrogen.

JOHNS HOPKINS UNIVERSITY,
March 14, 1906.

REPORTS.

The Atomic Weight of Nitrogen.

In the last report, for 1906, of the International Committee on Atomic Weights, attention is called to recent work on chlorine and nitrogen which indicates that an entire revision of the atomic weights may soon be necessary, because nearly all of them are based on the assumed accuracy of a few, such as those of silver, chlorine, bromine, sodium, etc., some of which have been changed as a result of the use of improved and more accurate methods. In the report refer-

ence also is made to the fact that nearly all the weights are based on the analyses of several oxyhalogen salts. "Their accuracy is assumed and all the anomalies, which appear in determinations based upon other lines of research, are commonly ascribed to undiscovered errors. The assumption may be sustained, but it is not yet beyond the reach of criticism." Among the atomic weights which have been redetermined by the more accurate and logical methods is that of nitrogen. The results obtained by independent workers, using different substances and both gravimetric and volumetric methods, necessitate the acceptance of the value 14.01 instead of the value 14.04, as found by the indirect gravimetric methods, and as adopted by the International Committee on Atomic Weights. This work upon the atomic weight of nitrogen has been carried out by Guye¹ and his colleagues at Geneva, and by Gray,² in Sir Wm. Ramsay's laboratory and in the Chemical Institute in Bonn. The basis of the present report is a lecture on the subject delivered by Guye, last year, before the chemical society of Paris. The fact is pointed out that, in the methods used by Stas and his predecessors and followers, as shown in Table I., the values are not very concordant and are generally higher than the values in Table II., which are based upon determinations of the densities of the gases, corrected by physical-chemical methods.

Table I.—From Chemical Data.

			Atomic weight.
Marignac	(1843)		14.043
Stas	(1865)		14.055
Dean	(1900)	ratio AgCN : Ag	14.031
Scott	(1901)		14.010
Thomsen	(1894)	" HCl : NH ₃	14.021
Hardin	(1896)	" Ag : AgNO ₃	14.01
Richards	} (1904)	" CsNO ₃ : CsO ₂	14.037
and		" KNO ₃ : K ₂ O ₂	14.040
Archibald			

Table II.—From Physical Data.

		Gases compared.	Method of correction.	Atomic weight.
Rayleigh	(1905)	N ₂ and O ₂	Limiting densities	14.009
		N ₂ O " O ₂	" "	13.996
Berthelot	(1898)	N ₂ " O ₂	" "	14.007
Leduc	(1897)	N ₂ " O ₂	Molecular volumes	14.005
Jaquero	} (1905)	N ₂ " O ₂	Comparison at high temperatures	14.008
and Perrot				

¹ Bull. Soc. Chim., [3], 33, 44 (1905).

² J. Chem. Soc., 87, 1601 (1905).

Guye points out that the methods which have been used in determining the atomic weight of nitrogen gravimetrically introduce a number of uncertain factors, and increase the probable error of the result. Thus, in the case when the value is determined from a study of the ratio $\text{Ag} : \text{NH}_4\text{Cl}$, he shows that the atomic weight determined can be expressed by the following equation :

$$X = Ar - B.$$

When r is the ratio of the silver and ammonium chloride, A the assumed known atomic weight of silver, and B the sum of the atomic weights of $4\text{H} + \text{Cl}$. While the value for r can be determined with considerable accuracy, those for A and B involve greater errors, especially as nearly all of the atomic weights are based on that of silver, and an error here would produce a greater error in the atomic weights of the other substances whose weights have been determined by reference to it. Guye concludes that the errors in the atomic weight of nitrogen, as determined by the classical methods of Stas and his predecessors and followers, vary from ± 0.013 to ± 0.039 , and that these methods cannot be used to determine the atomic weight of nitrogen with accuracy in the second decimal place.

On the other hand, by the use of modern physical-chemical methods, very concordant and accurate determinations can be made. These values are obtained by determining the ratio of the density of nitrogen to that of other gases, the results being then corrected with due regard to the laws of Boyle, Avogadro, etc. The methods used to correct the densities found are :

- (a) The reduction of the critical constants ;
- (b) The method of limiting densities ;
- (c) The method of corresponding densities ;
- (d) The method of the molecular volumes.

In this manner results are obtained in which the error is only ± 0.003 .

The atomic weight of nitrogen as determined by these methods is 14.008, as shown by the following summary of the results :

Ratio of	N_2	and	O_2	(6 determinations)	14.009
" "	N_2	"	CO	(6 ")	14.006
" "	N_2O	"	CO_2	(2 ")	14.007
" "	NO	"	O_2	(2 ")	14.008
General average,					14.008

While the older gravimetric methods used to determine the atomic weight of nitrogen are not accurate, owing largely to their unfortunate selection, it is possible to choose substances where both the direct weights and volume relations can be determined in the same substance.

Guye has thus been able, using nitrous oxide, to determine the atomic weight of nitrogen by the two methods. A glass tube, containing a spiral of iron wire, connected by platinum loops fused in the ends of the tube, is first exhausted and weighed, then filled with pure dry nitrous oxide and weighed. If a current is then passed through the spiral the gas is decomposed and the nitrogen formed is absorbed in a tube of coconut charcoal, which has been carefully exhausted. The weight of the nitrogen can thus be determined, as can that of the oxygen, by the increase of weight of the tube containing the spiral. This, of course, is a very brief outline of the method and gives no idea of the immense difficulties which had to be overcome before it could be used. The average of one series of 5 determinations was 14.007, while another, of 3 determinations, gave 14.004.

In the analysis by volume the same apparatus was used to decompose the gas. The vessel, to which a manometer was attached, was filled with nitrous oxide, which, after its pressure had been determined, was decomposed. By observing the change in pressure, keeping the volume constant, the necessary data could be obtained from which to calculate the atomic weight. The mean of 4 determinations by this method gave 14.015, which, averaged with the analyses by weight, gives a mean of 14.009, as compared with the atomic weight 14.008 by the physical-chemical method.

Analysis by weight of N_2O (5 determinations)	14.007
“ “ “ “ “ (3 “)	14.003
“ “ volume “ “ (6 “)	14.015
	<hr/>
	14.009

That this figure or, in round numbers, 14.01, is more correct than 14.04 is confirmed by the work of Gray, who used nitric oxide, which was obtained free from nitrous oxide and nitrogen. The nitrous oxide was removed by allowing the impure nitric oxide gas to bubble through several vessels containing liquid nitric oxide in which the nitrous oxide was absorbed. The nitrogen was separated by subliming the nitric oxide containing nitrogen at a low pressure and removing the nitrogen, which was not absorbed under these conditions, by the pump.

The gas thus obtained was carefully tested for impurities, its density was determined and the value corrected to reduce it to that which it would have as a perfect gas, and also to obtain the atomic weight of nitrogen by the gravimetric method. The apparatus used by Gray consisted of a vessel which could be exhausted, it contained a porcelain boat resting upon nickel supports; these served as the two poles of a source of electricity which was used to heat the contents of the boat by means of a platinum wire wound around the boat and connected with the nickel wires. Carefully purified nickel, in a finely divided condition, was placed in the boat. The known weight of nitric oxide could be decomposed by contact with the heated nickel, the free nitrogen absorbed in charcoal and weighed, and the oxygen determined by the increase in weight of the bulb and boat.

The results obtained by this method may be summarized in the following table :

I. From the density of nitric oxide corrected by two different methods, 12 results	14.006
II. From the density of nitrogen gas obtained in the gravimetric analysis, 2 results	14.008
III. From the gravimetric analysis of nitric oxide, 22 results	14.010
<hr/>	
General average, giving each result an equal value	14.0085

From an examination of Tables I. and II. it will be seen that the physical-chemical methods give, in general, more concordant and lower results than the chemical methods. Guye suggests that possibly this may be due to an error in the atomic weight of silver and presents the following arguments in favor of a lower value :

Recalculating 60 determinations of the ratio of silver to silver salts, using the figure 14.01 for nitrogen, the average result for silver is 107.885.

While the atomic weights of carbon, nitrogen and hydrogen have been accurately determined by the physical-chemical methods, those of chlorine, sulphur and phosphorus have been obtained by the use of only one gas in each case, and the results have not yet been verified. If these weights are used to recalculate a number of determinations, an average of 107.905 is obtained for silver.

Dixon and Edgar have determined the atomic weight of chlorine by a direct synthesis of hydrochloric acid, from hydro-

gen and chlorine; they obtain the value 35.463. The use of this weight in the recalculation of the atomic weight of silver gives the figure 107.88.

From a consideration of all these facts Guye suggests that the difference in the atomic weight of nitrogen, as obtained by the older gravimetric methods and by the physical-chemical methods, may be due to the use of too high an atomic weight for silver, which probably lies between 107.871 and 107.895, and cannot be as high as 107.93, the value adopted by the Committee on Atomic Weights.

J. E. G.

The Action of Ozone on Organic Compounds.

Since the discovery of ozone by Schoenbein, in 1840, its action on various organic substances has been investigated by a considerable number of chemists. The results, hitherto, have not been very satisfactory, nor have they led to conclusions of general interest. This has arisen, in part, from the difficulty of obtaining ozonized oxygen of sufficiently constant composition and with the necessary concentration of ozone, in part, however, from the explosive nature of the products of the reaction. The results may be summarized by saying that ozone was known to act on various hydrocarbons such as methane and ethylene, and on alcohol, forming aldehydes, acids and hydrogen peroxide, while, under certain conditions, explosive products of the nature of peroxides were formed, which were decomposed by water in a highly complicated fashion.

Some time ago C. Harries, professor at the University of Kiel, noticed how readily ozone attacks rubber, a fact which is well known to all who have worked with ozone, but on treating pure caoutchouc with it he obtained no reaction. By means of an alternating current of high voltage, the ozone content of the gas was raised to about 5 per cent; this gaseous mixture readily acted on caoutchouc, but the product is too complicated to be of service, at present, in the elucidation of the constitution of the parent substance.

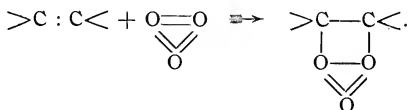
Harries, in conjunction with a number of co-workers, then investigated, in a systematic manner, the action of ozone on various classes of organic compounds; most of the results have been published, at intervals, in brief papers, but recently they have been embodied in a single article¹ of considerable interest.

The experiments were carried out by dissolving the substance under examination in most carefully dried chloroform, cooling the solution in a freezing mixture and passing through it a stream of ozonized oxygen and carbon dioxide. The lat-

¹ Ann. Chem. (Liebig), 343, 311.

ter serves to remove volatile products and to diminish the danger of explosion. The chloroform appears to have a similar influence.

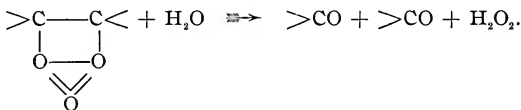
In these circumstances ozone is found to combine with compounds containing an ethylene linkage, forming "ozonides," a term which has been applied previously by Schoenbein to silver peroxide :



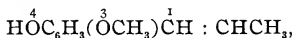
It will be noticed that Harries formulates the oxygen as tetravalent, neither the reason nor the necessity for this is wholly apparent ; the results could be equally well expressed by an ordinary bivalent form, and, indeed, the author is not consistent in the use of his tetravalent formulæ.

Ozone is without action on the trimethylene ring.

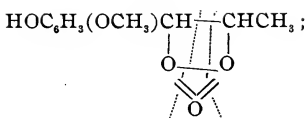
These ozonides are, in general, thick oils, or colorless, vitreous syrups, they have a characteristic, disagreeable odor and are more or less explosive. Some of them can be distilled under reduced pressure, others are resolved into their constituents when heated and the remainder explode. That they are peroxides is shown by their liberation of iodine from potassium iodide and their bleaching of indigo and potassium permanganate solutions. The most interesting reaction of the ozonides is, however, their behavior with water, in contact with which they yield hydrogen peroxide and aldehydes or ketones :



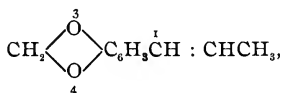
These reactions explain the production from isoeugenol,



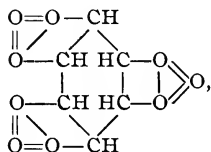
of vanillin by the action of ozone and water, the primary product being the ozonide, which decomposes in the manner indicated,



isosaftrol,

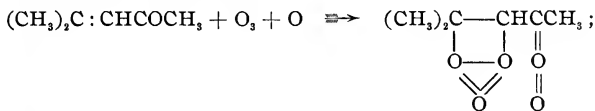


yields, in a similar manner, piperonal. With benzene the triozonide,

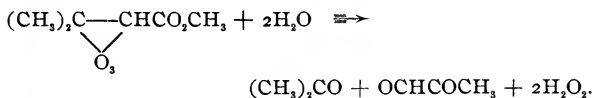


is formed which, with water, gives $3\text{HCOCHO} + 3\text{H}_2\text{O}_2$. It is many years since a more beautiful, purely chemical support for the Kekulé formula has been furnished.

Ethylene compounds containing a carbonyl group, *i. e.*, unsaturated aldehydes, ketones and monobasic acids, when treated with ozone, combine with 4 atoms of oxygen, as shown with mesityl oxide, for example :



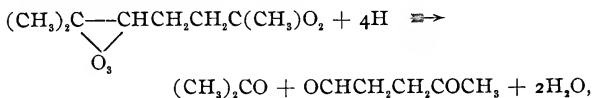
with water the decomposition is similar to that already described,



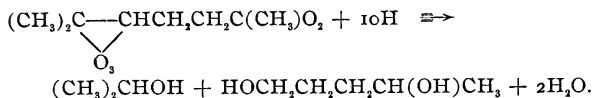
In some cases the decomposition takes a different course, resulting in the production of peroxides, such as acetone peroxide, $(\text{CH}_3)_2\text{CO}_2$. This capacity of carbonyl derivatives to

decompose ozone, in contradistinction to the ability of the carbon atoms with an ethylene linkage to add it, is not confined to unsaturated aldehydes and ketones, heptoic aldehyde (œnanthol), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$, for example, with ozone, yields the peroxide, $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{O}:\text{O}$, which is isomeric with heptoic (œnanthic) acid and, indeed, changes spontaneously into this in the course of time; with water the peroxide yields hydrogen peroxide and regenerates the original aldehyde. It is obvious that these facts are highly important and suggestive in connection with the current theory of the conversion of aldehydes into acids.

The action of nascent hydrogen on the ozonides is dependent on the proportion of the former; this is illustrated by methylheptenone ozonide, which, in ethereal solution, with aluminium amalgam, gives acetone and lævulinic aldehyde, or the corresponding alcohols, as follows:

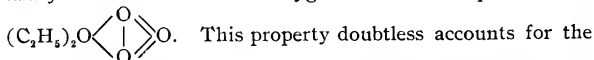


and



The preceding facts make it easy to understand some of the results obtained by earlier workers, such as the formation of formaldehyde and formic acid from ethylene and ozone, and it is possible to correct certain statements which have found their way into the literature; thus, the ozone derivative of benzene is, as has been stated, $\text{C}_6\text{H}_6\text{O}_9$ and not $\text{C}_6\text{H}_6\text{O}_6$.

Ether appears to be capable of absorbing an unlimited quantity of ozone, the product is a viscid, colorless liquid, which may be distilled under reduced pressure, but which often explodes with terrific violence. These explosions are, apparently, spontaneous. No formula can be assigned to this substance, as the analytical results were very variable, but it certainly contains much more oxygen than the simple ozonide,

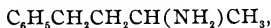


violent explosions which occur from time to time during the distillation of ether, in circumstances where all suspicion of

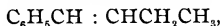
the ignition of an ether vapor—air mixture is excluded, for we know that ozone is produced in the laboratory by various processes which are operative there.

By means of ozone Harries has succeeded in preparing, with ease, a number of interesting compounds which were either previously unknown or difficult to obtain; the list includes lævulinic aldehyde, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$, from methylheptenone; aminoacetaldehyde hydrochloride, $\text{OCHCH}_2\text{NH}_2\cdot\text{HCl}$, from allylamine hydrochloride; succinic dialdehyde, $\text{OCHCH}_2\text{CH}_2\text{CHO}$, from diallyl; methylglyoxal, OCHCOCH_3 , from mesityl oxide, and mesoxaldialdehyde, OCHCOCHO , from phorone.

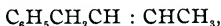
One of the most interesting sections of Harries' paper is that which deals with the results of his efforts to apply the ozonide reaction to the determination of the constitution of various compounds. Space will not permit of details being given, but the ground for his conclusions will be readily understood by the contents of the preceding paragraphs. The phenylbutene obtained from 1-phenyl-3-aminobutane,



proves to be a mixture of 1-phenylbutene(1),



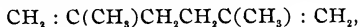
and 1-phenylbutene (2),



because it yields a mixture of benzaldehyde and phenylacetaldehyde. Diallyl must contain its ethylene linkage in the 1,5-position, because it yields succinic dialdehyde,



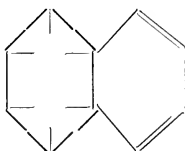
The hydrocarbon formed from magnesiummethyl iodide and diethyl succinate is 2,5-dimethylhexadiene(1,5),



because it yields formaldehyde and acetyl acetone. Dimethylheptadiene is $(\text{CH}_3)_2\text{C} : \text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3) : \text{CH}_2$, because it yields lævulinic aldehyde and, for the same reason, the fundamental hydrocarbon of caoutchouc has the identical grouping, *viz.*, $>\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)<$. Crotonic and isocrotonic acids, $\text{CH}_3\text{CH} : \text{CHCOOH}$, must have the same constitution because both yield acetaldehyde and glyoxalic acid, and a similar relation is proved to be true of oleic and elaidic acids,

$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, each of which gives nonylic aldehyde, $\text{CH}_3(\text{CH}_2)_7\text{CHO}$, and the half aldehyde of azelaic acid, $\text{OCH}(\text{CH}_2)_7\text{COOH}$. The results with compounds of the terpene series were not so simple and are being further investigated.

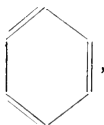
The action of ozone on benzene has been described earlier in this report. Mesitylene, in a similar manner, yields methylglyoxal, CH_3COCHO . From naphthylene a diozonide is formed which yields phthalic dialdehyde, $\text{C}_6\text{H}_4(\text{CHO})_2$ and, probably, glyoxal; this is regarded as supporting ~~Bamberger's~~ formula for naphthalene,



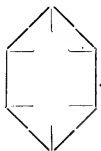
see errata
p. 570

according to which one ring is "aliphatic" and the other "aromatic." Phenanthrene behaves in a manner similar to naphthalene, but anthracene could not be investigated on account of its insolubility. Diphenyl gives a tetraozonide.

The author suggests that those aromatic compounds which react with ozone probably have ethylene linkages in the nucleus.



whereas nitrobenzene, chlorobenzene, phenol ethers, acids, esters, etc., which are indifferent to ozone, are represented by the centric formula



The paper is extremely interesting and well worth the study of all chemists.

J. BISHOP TINGLE.

The Physical and Chemical Properties of Iron Carbonyl.

There has recently¹ appeared, under the above title, a paper by Sir James Dewar and Dr. Humphrey Owen Jones, which forms a sequel to those by the same authors on nickel carbonyl.² Attention is directed more particularly to the differences in formula, color, stability and, especially, in behavior toward light between the analogous compounds of iron and nickel.

Iron pentacarbonyl was discovered in 1891 by Mond and Quincke,³ and was shortly afterwards isolated and studied by Mond and Langer,⁴ to whom our knowledge of this remarkable substance is almost entirely due. This is owing, no doubt, to the great difficulty in obtaining the compound in quantity sufficient for investigation, a drawback which has not yet been overcome.

Iron carbonyl is a yellow liquid, the color being retained even after careful purification and drying; its formula is $\text{Fe}(\text{CO})_5$, as proved by analyses and molecular weight determinations.

The vapor of iron pentacarbonyl was found to decompose quietly, without explosion, when heated to high temperatures alone, or in an inert gas. In general, its chemical reactions are exactly parallel with those of nickel carbonyl, differing only in their rapidity, which is much less owing to the greater stability of the iron compound. There are, however, some exceptions to this behavior.

The most striking difference between the two compounds is the decomposition of the iron derivative by light. This was observed by Mond and Langer, who gave to the solid product of decomposition the formula $\text{Fe}_2(\text{CO})_7$, but their compound was not pure.

Dewar and Jones observed that, when pure, this solid substance shows no change upon exposure to dry air, and is only slowly affected by ordinary air; but that, if the decomposition of the liquid carbonyl is incomplete and the solid is contaminated with the liquid compound, it often takes fire.

By exposure of the ether or petroleum ether solution of the liquid carbonyl to light, pure crystals of the solid carbonyl were obtained as beautiful, lustrous, hexagonal, orange col-

¹ P. Roy. Soc., **76**, 558 (1905). Chem. News, **93**, 1, 14, 24 (1906).

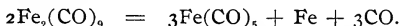
² P. Roy. Soc., **71**, 427 (1903). J. Chem. Soc., **85**, 203, 213 (1904).

³ J. Chem. Soc., **59**, 604 (1891).

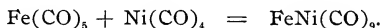
⁴ *Ibid.*, **59**, 1091 (1891).

ored plates. An analysis and a study of the liquid carbonyl established the formula $\text{Fe}_2(\text{CO})_9$ for these crystals.

Upon being heated to 100° the nonacarbonyl decomposes according to the equation :



Of considerable interest are the solutions of iron carbonyl in nickel carbonyl. These exhibit a much paler yellow color than solutions of equal concentration in other solvents. Moreover, light does not cause decomposition of the iron carbonyl when it is in dilute solutions in nickel carbonyl. To account for these facts the authors suggest the formation of an unstable compound,



E. J. HOFFMAN.

REVIEWS.

ÉTUDE GÉNÉRALE DES SELS. Par ALFRED DITTE, Membre de l'Institut, Professeur de Chimie à l'Université. Première Partie, Sels Binaires. Prix, 10 Francs. Deuxième Partie, Sels Ternaires Oxygénés. Prix 12 Francs 50. Paris : Dunod et Pinat. 1906.

These beautifully printed volumes are, perhaps, the most important recent contribution to the general literature of inorganic chemistry. Especially is the first volume important. Much of the chemistry of binary compounds is recent and is not found in text-books. Most of this new work is from Moissan and his pupils, often done with the help of the electric furnace at very high temperatures, or at extremely low temperatures with the agency of liquid air. Hitherto, knowledge of this work had to be pieced together from scattered, brief articles in the *Comptes rendus*. In this first volume—a large book of 304 pages—the author considers, in detail, the following binary series: Hydrides, fluorides, chlorides, bromides, iodides, cyanides, oxides, sulphides, selenides, tellurides, nitrides, phosphides, arsenides, antimonides, carbides, silicides and borides.

If the reader realizes that he, like most other chemists, really knows nothing of half of the compounds on this list, and that Ditté devotes 13 pages to hydrides, 18 to fluorides, 14 to cyanides, 9 to selenides, 16 to nitrides, 20 to carbides, etc., it is clear that here is something to be studied by older chemists as well as by advanced students, and that here the material, hitherto accessible only to those who could consult large libraries, is offered to the chemist in clear, well-classified form.

The second volume, of 383 pages, is in two sections. In the first the subjects are : General properties of salts, the action of heat, of light, of electricity upon salts, the action of the inherent mechanical energy of salts (explosives and explosion waves), the action of metals, of water, of other liquids than water, of oxidizing and reducing agents on salts, the reciprocal action of acids, bases and salts (theories of affinity), the action of acids, of bases and of salts upon salts. In the second section the author applies these studies to definite classes of salts: Nitrates, chlorates, sulphates and carbonates are the series chosen.

Those not accustomed to reading French books on inorganic chemistry will be struck by the fact that every chemical change is expressed—every equation written—in the terms of Berthelot's thermochemical system, and that no mention whatever is made of ions or electrolytic dissociation in the first volume, and in the second volume in two places only ; first in a few absolutely necessary lines to explain the action of electric currents on bases and salts, and second in the admirably clear chapter on the action of water on salts, which includes the properties of solutions. Here 40 pages are given to the work of Faraday, Raoult, Coppet, Arrhenius, Jones, Nernst, Abegg and Loomis.

Still less will the structural chemist find his accustomed diet. In the chapter on sulphates the only reference to the subject of water of crystallization and water of constitution, or tetrahydroxylsulphuric acid, is the brief, bald statement, without data, that water combines with many sulphates to form hydrates which lose the water at varying temperatures, leaving anhydrous sulphates.

It is instructive to see how nicely a structuralist, an ionist, or a thermochemist can severally express the same facts, each ignoring all of the sacred dogmas of the other two, and calling especial—often exclusive—attention to those properties which are brought into relief by his views, or which bring his views into relief. For a layman the thermochemical view is, perhaps, the easiest of the three to crudely understand, on account of the incessant harping on thermal values only. This is very convenient as regards this book, for it enables the structuralist or ionist, who is quite unfamiliar with the Berthelot brand of thermochemistry, to get at the more important facts, postponing theories until some one of his own school may rewrite the material in terms of the desired theory.

A quotation from Vol. II., page 3, illustrates the French

point of view. The author has spoken of Gerhardt and his type theory.

" . . . Following the discovery of the polyatomicity of phosphoric acid, glycerin, the sugars, etc., Gerhardt's disciples were led to resurrect the theory of radicals, treating it in an extraordinary way; to explain this curious property they imagined the existence of fictitious, unsaturated radicals—hydroxyl, carbonyl, sulphuryl, etc., and soon extended the idea of saturation or atomicity to the elements themselves, which were classified as mono-, bi- and triatomic. Typical formulas gradually gave place to so-called constitutional formulas, in which figure imaginary bonds between different elements and different hypothetical radicals.

"The formulas of salts represent nothing further than one of their modes of generation.

"All these metaphysical considerations have but a secondary interest from the point of view that the study of chemistry should not lie in discussing properties lying outside of the sphere of verified observation No method of writing the formula of a salt can indicate the inner structure, *for this escapes us, if, indeed, it exists.* A salt, like any other object, is a form of matter—nothing more, nothing less. If we write sulphate of zinc SO_4ZnO , we are expressing the fact that the easiest way to make it is by the action of sulphuric acid on zinc oxide; and when we write $\text{SO}_3 \text{ sol.} + \text{ZnO sol.} = \text{SO}_4\text{ZnO sol.} + 41.3$, we express, apart from all theory, the experimentally proved fact that, in passing from the system formed by solid sulphuric acid and solid zinc oxide to the solid sulphate of zinc, one must modify the velocity of these first two forms of matter so as to make them lose an amount of energy measured as 41.3 calories, and that, in consequence, the sulphate of zinc differs from the mixture of acid and base *solely and alone by this loss of 41.3 calories.* The formula SO_4Zn expresses the fact that this sulphate may be made by combining sulphur, oxygen and zinc in the indicated weight—proportions, and the equation $\text{S} + \text{O}_4 + \text{Zn} = \text{SO}_4\text{Zn sol.} + 229.6$ expresses the experimentally proved fact that solid sulphate of zinc differs from the system which represents the sum of its component elements solely and alone through a loss of energy measured by 229.6 calories."

To the reviewer, and doubtless to others trained in the Kekulé school, such ideas are unacceptable and, indeed, revolting; let us remember that the French chemist finds carbonyl and hydroxyl revolting, and that men trained to think in the French school have found in these views the stimulus

See Chapter 570

to work of the very highest permanent value. To us there is an undoubted benefit in approaching a known subject by a new road.

In these volumes of Ditte we find the scholarly treatment of the subject, the limpid clarity of diction and the complete literary finish which we have learned to expect from men of science in France.

E. R.

LABORATORY EXPERIMENTS TO ACCOMPANY OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and CLAUDE FREDERIC WALKER, Teacher of Chemistry in the High School of Commerce of New York City. New York: The Macmillan Co. 1905. Price, 50 cents.

This is an interleaved manual and note-book to be used with Gooch and Walker's "Outlines of Inorganic Chemistry," which was recently reviewed.¹

E. R.

HANDBOOK OF METALLURGY. By C. SCHNABEL. Translated by H. LOUIS. Vol. I. London and New York: Macmillan & Co., Limited. 1905. Price, \$6.50.

In the study of non-ferrous metallurgy the English-speaking student has always been at a disadvantage in comparison with the French, and especially the German, in that he had to work without a book covering the subject adequately. As the standard German handbook of the late Bruno Kerl appeared as early as 1881, even Germans had to content themselves with the smaller publications of Balling and Pufahl to cover the more recent developments of practice until Schnabel published his two-volume "Handbuch der Metallhüttenkunde" in 1894 and 1896. This was translated by Louis and brought out in 1898 and Of this revised and enlarged German edition of 1901-1903, the translation of Vol. I., the subject of the present review, has been again brought out by Louis. It covers the metallurgy of copper, lead, silver and gold. Volume II., treating of the minor metals, is promised for 1906. A student accustomed to follow the literature of non-ferrous metallurgy fails to find much that is new in reading Schnabel's manual; on the contrary, he sees little more than what he has become familiar with in other books. While this is a disappointment, the book, nevertheless, deserves praise because the principles of the various processes and operations are brought out clearly and their applications discussed by numerous examples from practice. The matter is well arranged, classification has, perhaps, been carried a little too far, and there may be too much repetition. The work has proved itself to be acceptable and to meet a certain demand, as is shown by the issue

¹ THIS JOURNAL, 34, 588 (1905).

of a new edition after a comparatively short interval of 7 years. The English volume has grown from 876 to 1090 pages; of this increase, 95 pages fall upon copper, 27 upon lead, 45 upon silver and 57 upon gold. The translation is all that could be desired. As to the size of the book, it appears to be too short to be exhaustive and too long to represent an ordinary text book. Authoritative criticism could not well be expected, as the time has passed when a single author could write a critical handbook on non-ferrous metallurgy. The future belongs rather to the compilers who, with the references, bring together all available facts leading to the first sources of information, and to the specialists who critically review all that is known in their several fields.

The German book, as it stands, supplements, to a certain extent, the treatise of Kerl; the translation, representing the only work of the kind, has the field to itself.

H. O. HOFMAN.

DIE MIKROSKOPIE DER TECHNISCH VERWENDETEN FASERSTOFFE.
Bearbeitet von DR. FRANZ RITTER v. Höhnel. 2te Auf., pp. 248, mit
94 Holzschnitten. Wien u. Leipzig: Hartleben. 1905.

The first edition of this work, which appeared in 1887, was one of the earliest attempts to systematize and co-ordinate the scattered papers bearing upon the microscopic characteristics of those fibers having industrial uses, and included the individual investigations of the author himself. These had largely extended our knowledge of the subject at that time, but the improvements in microscopical methods, together with the appearance of various new fibers in the arts during the 18 years since the earlier edition, has made an extended revision necessary. The use of polarized light and the study of the dichroitic properties, aided by more numerous and better methods of staining, have added materially to the knowledge of the structural characteristics of many fibers, and the microscope has acquired increased importance in the technical examination and valuation of textile and other products.

The subject is considered under three heads: Vegetable Fibers, Animal Fibers, Wool and Hairs and Silks. In the 6 pages of introduction the scope of the work is outlined, and notes are given concerning the necessary instruments and reagents required for the study of fibers. Then follow about 24 pages of general statements concerning vegetable fibers, their morphological character, their microchemical and microphysical properties, and 2 tables showing the lengths and diameters of all the common vegetable fibers. In the next section the general structure of wool and hair is considered, together with the

methods of study and microchemistry and, lastly, the special examination of the individual species. Some 15 animal fibers are described and illustrated. The chapter on silk, following the same general scheme of treatment, consists almost wholly of the results of investigations by the author, previously published, in part, in "Dingler's polyt. Journal," 246, 465.

The author holds that a mere description of a fiber is not sufficient to identify it with certainty, the real distinguishing features often being not superficially noticeable, but recognizable only by careful and painstaking *comparisons*. The precautions necessary in observation and treatment of fibers under examination are clearly set forth, with descriptions, illustrations and comparisons of the industrially important fibers. Throughout the entire text the cuts, 94 in number, are of noticeable clearness in outline and detail, and appear to be from drawings made from the *camera lucida*. But the clearness and simplicity of the *camera lucida* picture is rarely observed in the actual microscopic field, where broken and crushed particles of fibers, indefinite masses of mucilaginous or protoplasmic matter, starch granules, epidermal and parenchyma cell tissue, lignified tissue and other bodies often become disturbing and obscuring factors in the study of the particular fiber sought. With the great improvement in modern photographic methods and the highly finished papers of to-day, at least a few photomicrographs and illustrations of polarized light effects would have added to the value of the work. The book will be of much assistance to microscopists and chemists having to deal with textile problems involving the identification of fibers.

F. H. THORP.

A TEXT-BOOK OF CHEMISTRY FOR THE USE OF STUDENTS AND PRACTITIONERS OF MEDICINE, DENTISTRY AND PHARMACY. By WILLIAM RUSSELL JONES, M.D., PH.G., Professor of Medical Chemistry and Toxicology, and Lecturer on Medical Diagnosis in the University College of Medicine, Visiting Physician to the Virginia Hospital, Richmond, Virginia. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1905. Price, \$2.50.

This volume is broad in scope. An introduction on the properties of matter is followed by a section on physics, 55 pages, giving elementary notions of gravity, heat, light and electricity. Then comes chemical philosophy, 23 pages; inorganic chemistry and qualitative analysis, 149 pages; organic chemistry, 125 pages; quantitative analysis, 5 pages; and physiological chemistry, 70 pages; a total of 448 pages.

The treatment is necessarily brief and elementary, but it is clear, and the book really includes what is necessary for dentists and pharmacists and for the average student of medicine.

It seems to the reviewer that the comprehensive plan of the book is very suitable, and that the chance of the average student acquiring a little definite knowledge of the different subjects is greater than if he were given separate text-books containing matter which he probably could not understand and certainly could not master in the time available. E. R.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry, Toxicology and Pediatrics in Long Island College Hospital, etc. Sixth edition. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 774. Price, \$3.00 net.

The author here presents a work dealing with the entire field of chemistry—organic, inorganic, physiological and theoretical. In addition to this, 67 pages are devoted to elementary physics. Those substances of medical and pharmaceutical interest are considered in greater detail, and often a brief statement of the physiological action is given. Under the important poisons the symptoms, antidotes and method of treatment are detailed. Several errors were noted in the book. Thus, the author defines an atom as "the smallest conceivable portion of matter." To this he adds the correct definition, but the student would have already received the wrong impression. Again, he states that "nitrogen may be tested for (in organic substances) by burning the substance in air, when, if nitrogen be present in more than traces, it will give off an odor like burning feathers or horn."

The arrangement is often very illogical indeed. Thus, in the part on organic chemistry, which consists of about 200 pages, the carbohydrates are considered and their structure given before the simple aldehydes and ketones have been described. The work may be of value, as a reference book, to physicians and pharmacists who must be satisfied with a single book on all chemical matters. A. S. L.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the University of Illinois.

THE REACTION OF NITROUS ANHYDRIDE WITH ETHYL MALONATE.

BY RICHARD SYDNEY CURTISS.

Many years ago Conrad and Bischoff¹ studied the reaction of these two substances in the presence of sodium ethylate. They passed the red gases, formed by the action of nitric acid and arsenious anhydride, into ethyl malonate, dissolved in alcohol containing 1 atom of sodium. When the solution became saturated with the gas and showed only a slight alkaline reaction, they precipitated an oily product by diluting it with water. They attempted to purify this oil by washing it with water and subjecting it to fractional distillation in a vacuum. This process decomposed the substance. They then simply washed the oil with water and dried it. The analytical results correspond well with the formula $\text{HON} : \text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, that of ethy isonitrosomalonate.

They found the yield of oil variable and never over 50 per cent of the ethyl malonate used. I have recently had occasion to use the ketonic ester, ethyl oxomalonnate, $\text{OC}(\text{CO}_2\text{C}_2\text{H}_5)_2$,

¹ Ann. Chem. (Liebig), 209, 211.

and the related crystalline body, ethyl dihydroxymalonate, $(\text{HO})_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, in considerable quantities, and have found the older methods of preparation described by Beilstein¹ very costly in material, time and labor. The following procedure overcomes these difficulties and gives a yield of 90–95 per cent of the pure esters, with very little expenditure of time or material. It is also superior to the methods described more recently by Bouveault and Wahl² and Schmidt.³ It is somewhat similar to the above process, whereby Conrad and Bischoff obtained ethyl isonitrosomalonate, no sodium ethylate is used, however.

The so-called nitrous anhydride was generated by the action of warm nitric acid, sp. gr. 1.42, on arsenious oxide, conducted through a flask to condense moisture and, without drying, passed in a rapid stream into 50 grams of ethyl malonate, at 0° , the latter substance being contained in a distilling flask, immersed in a freezing mixture. The gas is extremely soluble in the liquid. Very little heat is generated in the reaction. A rapid stream of the gas is completely absorbed for three quarters of an hour. The operation was then stopped, 58 grams of gas had been absorbed. The pale blue color first formed rapidly changes to a dark green, almost opaque at the last. The flask and contents are allowed to remain in the ice mixture for several hours at 0° , then to slowly assume the temperature of the room, and remain thus for nearly 2 days, at 23° – 28° . As it warms, red gases are slowly evolved; the loss in weight, in 18 hours, is 11 grams, and after 40 hours, 14 grams. The total weight of the crude green oil at this stage is 94 grams. This green oil consists chiefly of the anhydrous and hydrated mesoxalic esters, together with small amounts of oxalic acid and ester, acetic acid and ester, and ethyl isonitrosomalonate.

At this point the process may be varied in 3 ways, dependent on the product wanted, whether ethyl oxomalonate (1), ethyl dihydroxymalonate (2), or the free mesoxalic acid (3).

(1) If the keto ester, ethyl oxomalonate, $\text{OC}(\text{COOC}_2\text{H}_5)_2$,

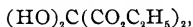
¹ "Beilstein's Handb. d. org. Chem." I., 788; Sup. I., 371.

² *Compt. rend.*, 137, 196.

³ *Ibid.*, 140, 1400.

is desired, the process of vacuum distillation is used on the crude oil. As the pressure is reduced the excess of red gases passes off, leaving in the flask a straw colored liquid, which distils almost entirely without destructive decomposition or darkening, leaving only 1-2 grams of thick, yellow syrup as residue. The first fraction (10 grams), passing over from 52° (70 mm.) to 70° (45 mm.) contains a little water, acetic acid and some esters. Then the distillate ceases, the temperature rises regularly from 70° to about 120° ; around 125° (70 mm.) a thick, amber-colored oil distils over, together with a little water. This mixture crystallizes in the receiving tube and consists of ethyl dihydroxymalonate. It is followed by the anhydrous ester, ethyl oxomalonate. This substance is the main product of the distillation. It passes over at 126° - 133° (42 mm.-50 mm.), (uncorr.) and weighs 55-60 grams.

(2) If the crystallized ethyl dihydroxymalonate,



is desired it may be readily obtained in two ways :

(a) The requisite quantity of water may be added to the above distillate of pure ethyl oxomalonate. This causes the temperature to rise to 45° ; it remains there while the liquid changes to a solid, crystalline mass of beautiful white plates. This is pure ethyl dihydroxymalonate, melting at 57° .

(b) The original crude, green oil, saturated with nitrous anhydride, may be poured into a large crystallizing dish and left exposed to the air. It loses thus its excess of absorbed gases, while it takes on atmospheric moisture, rising in temperature thereby, and slowly passes into a crystalline mass. This also, when filtered with the aid of a pump and well washed with carbon bisulphide, is practically pure ethyl dihydroxymalonate. It was recrystallized from ether, dried quickly in a vacuum over sulphuric acid and analyzed :

	Calculated for $(\text{HO})_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$.	Found.
C	43.75	44.19
H	6.25	6.58

The carbon appears somewhat high, owing to the fact that this substance loses water in a desiccator and changes to the ketonic ester, ethyl oxomalonate.

(3) If the free mesoxalic acid $(HO)_2C(COOH)_2$ is desired, it can be readily made from the crude oil as follows: Twenty-five cc. of this oil is extracted with 10 cc. of cold water, which dissolves its own weight of soluble products. A second extraction is made, but removes little soluble matter. This aqueous extract is placed in a crystallizing dish and evaporated in a vacuum desiccator, over sulphuric acid. A dry, crystalline mass of mesoxalic acid remains. This substance deliquesces in the open air, changing into a thick, colorless syrup. Placed again over sulphuric acid, it recrystallizes in the forms characteristic of dihydroxymalonic acid. Its identity is further shown by its melting-point, 115° – 116° , its ability to form insoluble calcium, barium and silver salts and, when mixed with phenylhydrazine and acetic acid, it yields a yellow body, which, recrystallized from alcohol, agrees in its melting point, 160° , and other characteristics with the phenyl hydrazone of dihydroxymalonic acid.

There is much that is misleading in the literature concerning ethyl dihydroxymalonate. The following properties of this substance have been noticed, in addition to those recorded by Beilstein:

The statement is made by this author¹ that ethyl dihydroxymalonate is insoluble in water. Conrad and Brückner² attribute this erroneous statement to W. Petrieff, and refer to his papers.³ No assertion whatever concerning the solubility of this substance is there made.

On the contrary, ethyl dihydroxymalonate is extremely soluble in water; 1 gram, at 22° , dissolves 1.3 grams of the substance, accompanied with a slight lowering of the temperature of the solution. One gram of ethyl malonate dissolves 0.6 gram of the crystals, a fact which has a decided bearing on the above method of separating it by crystallization. One cc. of benzene, at 22° , dissolves 0.2 grams of the ester. It is also

¹ "Handb. der Organ. Chem.," I., 788.

² Ber. d. chem. Ges., 24, 3000.

³ *Ibid.*, 8, 730; 11, 415.

easily soluble in ether, acetone, chloroform and absolute alcohol. It is slightly soluble in ligroin and insoluble in carbon bisulphide. Pure ethyl dihydroxymalonate is volatile in air at ordinary temperatures, and especially so in a vacuum. If a film of it be left on a watch-glass, in a current of air, it disappears entirely in 24 hours. It loses water in a desiccator, thereby changing to an oil, but it is quite stable in moist air at ordinary temperatures, and can be thus kept for months without decomposition. Only in an impure form does it slowly soften and liquefy. It can be distilled under reduced pressure (40-50 mm.) without any darkening in color, or any marked decomposition other than the loss of a molecule of water and the formation of the ketone form of the ester.

In a note¹ on the subject of this paper the more recently discovered reactions which produce mesoxalic esters were discussed and, among others, that of Bouveault and Wahl,² who produced it by the action of nitric oxide upon ethyl isonitrosomalonnate. They had also noticed that the latter ester was formed by the action of nitric oxide upon ethyl malonnate.

At the time that the above note¹ was printed, Schmidt,³ carrying out the ideas of Bouveault, presented to the French Academy a paper describing a process for making ethyl oxomalonate, by a combination of these two reactions. Nine hundred grams of dry sodium nitrite were mixed with 3000 grams of sulphuric acid, below 0°. The resulting nitrosyl-sulphuric acid was decomposed with water, and the nitric oxide passed into a mixture of 200 grams of ethyl malonnate, in acetic anhydride. The process was continuous for several days, then the liquid was distilled in a vacuum. A 65 per cent yield of a product was obtained, which had a boiling point of 95°-130° (15-25 mm.) and was called "ethyl mesoxalate." As this substance, ethyl oxomalonate, boils constantly at 126°-127° (45 mm.) (uncorr.), the above product, with a variation of boiling point of about 25° at constant pressure, must consist largely of other substances. The yield of pure ester is

¹ THIS JOURNAL, 33, 603.

² Compt. rend., 137, 196.

³ *Ibid.*, 140, 1400.

not given, nor that of the crystals of ethyl dihydroxymalonate, which form in the oil.

The process described in the present paper requires but 2-3 hours of the chemist's time, and gives a yield, on the ethyl malonate used, of 90 per cent or more of pure ethyl dihydroxymalonate (m. p. 57° - 58°). If desired, the yield can be raised above 95 per cent by repeating the process on the small amount of oil filtered off from the crystalline product.

The action of nitrous anhydride on ethyl malonate gives other products, in quantities varying widely with the conditions of temperature, moisture, degree of saturation with the gas and time of reaction.

Experiments in which a little water was added to the ethyl malonate and the gas then passed at 0° and allowed to stand a few days, gave a considerable quantity of acetic acid and ester. Oxalic acid crystallized out from the aqueous liquid at the bottom of the flask. The effect was, therefore, saponification of the malonic ester, loss of carbon dioxide and decomposition of ethyl mesoxalate, with formation of oxalic acid.

This change of ethyl oxomalonate to oxalic acid takes place slowly in the mixture, even in the absence of any considerable quantity of water, as shown by the following experiment: A loosely covered cylinder containing 21 cc. of ethyl malonate, was saturated with the gas and placed in the window in the sunlight. Crystals of oxalic acid began to deposit within a week. It was allowed to stand there 8 months and slowly lost gas during the entire time. The volume of oil decreased 50 per cent and was filled to the surface with balls of needle-shaped crystals. The various tests applied showed these to be oxalic acid.

If the ethyl malonate is only partially saturated with nitrous anhydride, ethyl isonitrosomalonate is present in considerable quantity, just as Conrad and Bischoff¹ discovered, when working with ethyl malonate in the presence of sodium and alcohol. Twenty-five grams of nitrous anhydride were dissolved in 50 grams of ethyl malonate, by passing the gas into the ester at 0° , for one-half hour. It then stood 32 hours at the ordinary

¹ Ann. Chem. (Liebig), 209, 211.

temperature. The initial blue color of the oil had changed to a pale, greenish yellow, and its weight was now reduced to 65 grams. Further exposure to the air caused but slight loss in weight. In a short time 17 grams of crystals of ethyl dihydroxymalonate were deposited. Twenty-eight grams of the mother liquor from these crystals were mixed with an equal volume of ether and washed with a few cc. of cold water, then with a saturated solution of sodium carbonate to alkaline reaction. The excess of alkali was removed entirely by water. The oil (A) which remained, after drying with calcium chloride and evaporating off the ether in a vacuum at 40° , was pale green, weighed 29 grams and had a fragrant, though rather pungent odor, resembling that of brominated fatty esters. It was slightly acid to litmus. This oil appears to be chiefly ethyl isonitrosomalonate.

This oil, 11.35 grams, was treated with 12.5 cc. of alcohol (96 per cent), which contained 1 mol. of potassium hydroxide. The alkali was added slowly and the temperature kept down to -10° . A yellow salt precipitated at once and was quite pure. If precipitated at ordinary temperatures gases are evolved and the product is impure. After standing 15 minutes, the cold mixture was filtered by means of a pump, washed well with alcohol and then with ether; 3.85 grams of salt were thus obtained. The yield is larger if absolute alcohol is used, as it is quite soluble in 95 per cent alcohol and especially so in water. The salt was twice recrystallized from hot, 95 per cent alcohol. It separates out on cooling in long, greenish-yellow needles. After drying in a vacuum, over sulphuric acid, it was analyzed. Potassium was determined as sulphate.

K	Calculated for	I.	Found.
	KON : $C(CO_2C_2H_5)_2$.		II.
	17.19	17.72	17.62

The salt dissolves easily in cold water, giving a yellow solution; it is fairly soluble in hot alcohol, slightly soluble in acetic ester, but insoluble in ligroin, chloroform and carbon bisulphide. Silver nitrate precipitates from its aqueous solution a beautiful yellow silver salt, which soon darkens in the

light. Copper acetate gives a flocculent precipitate, soluble on dilution with water.

The potassium salt, placed in a melting point tube, in a bath at 185° , slowly darkens in color; heated rapidly it contracts and decomposes, with frothing, at 195° – 200° . If, however, the dry salt be heated carefully in a test tube it reddens on the edges and suddenly explodes, with a flash of purple flame.

Conrad and Bischoff¹ confirm Baeyer's² observation that isonitrosomalonic acid, in aqueous solution, is decomposed at 40° , giving hydrocyanic acid, carbon dioxide and water.

I have been unable to obtain any test for hydrocyanic acid from the saponified ester, or from the products of the explosions of its potassium salt.

Attempts to make a sodium salt by the action of a 40 per cent aqueous solution of sodium hydroxide on a concentrated, ethereal solution of the oil (A) gave no precipitate, owing to the great solubility of this salt. On evaporating the solutions over sulphuric acid, however, a canary-yellow salt slowly crystallized out. It was not further purified. Neither could this salt be precipitated by the use of sodium hydroxide, dissolved in absolute alcohol.

Concentrated, aqueous ammonium hydroxide placed on the oil (A) gives a yellow solution, which, on evaporation in the air, deposits yellow crystals in the form of needles. This salt is unstable and soon turns red. Aniline reacts with the oil, giving a product which crystallizes in needle forms and is slightly soluble in alcohol and ligroin.

By neutralizing the sodium carbonate solution, which had been used in washing and purifying the above oil (A), with hydrochloric acid, 6 grams of a yellow acid oil were obtained. This was taken up in ether, the ether evaporated and the residual oil dried over sulphuric acid and solid potassium hydroxide. During the process of desiccation the alkali is coated bright yellow by some volatile substance.

A concentrated potassium hydroxide solution precipitates this oil, almost completely, in the form of a yellow potassium

¹ Ann. Chem. (Liebig), 209, 211.

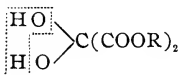
² *Ibid.*, 131, 293.

salt. A slight ammoniacal smell is apparent and the gas given off turns red litmus paper blue. The oil also forms a green copper salt with copper acetate solution. It was not further studied, but was assumed to be ethyl isonitrosomalonate.

The reaction of nitrous anhydride on methyl malonate will be studied to see if it will give an equally satisfactory yield of methyl oxomalonate, thereby removing these substances from the list of rare and expensive preparations, which, hitherto, could only be procured when specially made to order by Kahlbaum and others in Germany.

It might be mentioned that the above method of making ethyl hydroxymalonate furnishes an admirable experiment for a laboratory class in organic chemistry, while illustrating the rare exception to the general rule that a carbon atom can hold but one hydroxyl group, and that stability of the molecule, dissociation and association, are largely questions of temperature.

The pure, colorless crystals of ethyl dihydroxymalonate, placed in a dry test tube, need but be heated to their melting point, 57° , when the elements of water dissociate,



which fact becomes at once apparent as the drops of water condense in the upper, cold part of the test tube. There is a very marked change from the thin, colorless liquid first formed, on melting, to a green oil, ethyl oxomalonate, which remains at the bottom of the tube. If, now, the test tube be cooled, closed with a rubber stopper and tilted so that the two liquids come in contact, they reunite, there is an immediate loss of the green color, the temperature rises sharply and, on touching the colorless syrup on the sides with a glass rod, a remarkably beautiful and rapid crystallization starts and passes throughout the whole inner surface of the tube, yielding again the original crystalline mass. This experiment can be rapidly repeated many times with the same sample of substance.

The preparation also furnishes an interesting example of a

ketonic ester in its reaction with aniline, with which it readily yields ethyl dianilinomalonate, $(C_6H_5NH)_2C(COOR)_2$, a substance crystallizing in beautiful rosettes of colorless needles.

In studying the action of phenylhydrazine on ethyl oxomalonate it has been noticed that it does not give the expected yellow crystalline phenylhydrazon as does the free acid, and also the acid ester, but yields an amber-colored oil which has *acid* properties.

A canary-yellow potassium salt has been made from this oil by treatment with alcoholic potassium hydroxide. This salt is stable in dry air but is dissociated by water, yielding the original acid oil. These reactions are being investigated.

URBANA, ILL.,
Feb. 28, 1906.

FURTHER INVESTIGATIONS OF THE TWO CHLORIDES OF ORTHOSULPHOBENZOIC ACID.¹

BY PHILIP H. COBB.

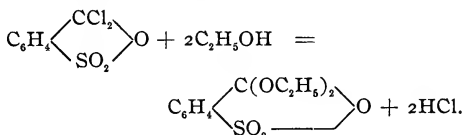
The earlier investigations of the two isomeric chlorides of orthosulphobenzoic acid have left a number of points unsettled and it was in the hope of clearing up some of these that, at the suggestion of President Remsen, I undertook the work, an account of which is given in this article.

I. The Action of Hydrochloric Acid on Organic Anhydrides.

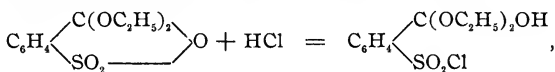
The action of alcohols on the low-melting chloride, in the cold, has been shown to consist in the formation of symmetrical ester chlorides, a fact which, taken by itself, would be a strong argument for the symmetrical structure of the chloride. In the light of the other evidence, however, it is plain that this reaction is not decisive, and in view of the fact that all of the distinguishing reactions show that the low-melting chloride is unsymmetrical, there must be some other explanation for the peculiar action of alcohol. It is always possible to assume a molecular rearrangement, but a more satisfactory hypothesis

¹ From the author's dissertation submitted June, 1905, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy.

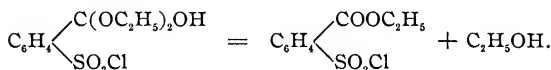
was suggested by Remsen.¹ The suggestion is this: When ethyl alcohol is allowed to act upon the low-melting chloride, the first step in the reaction would naturally be the substitution of two ethoxy groups for the chlorine atoms, thus:



The anhydride might then take up hydrochloric acid,



and the product thus formed would lose alcohol and pass into the ester chloride:



In order to test this view experimentally, the action of dry hydrochloric acid on various organic anhydrides was tried. Experiments of this kind have already been made with acetic,² benzoic,³ benzoic-acetic⁴ and some other acids, but no experiments with the anhydrides of dibasic acids or inner anhydrides have been recorded. It appears that the anhydrides of monobasic acids react readily with dry hydrochloric acid. Attention was now turned to the inner anhydrides.

From the experiments performed it is evident that the anhydrides of the dibasic acids studied do not react with dry hydrochloric acid, while those of monobasic acids are easily attacked. Therefore the formation of symmetrical ester chlorides, by the action of alcohol on the low-melting chloride, does not seem to be dependent upon the presence of hydrochloric

¹ THIS JOURNAL, 30, 247.

² H. Gal: Ann. Chim. Phys., [3], 66, 187.

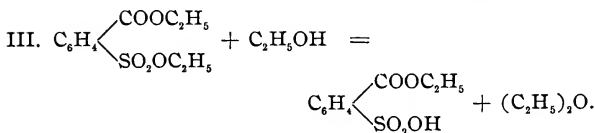
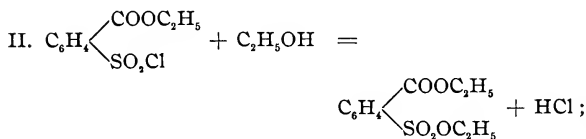
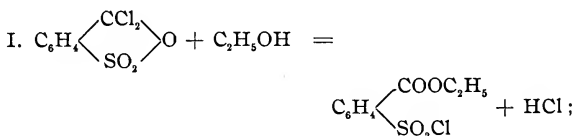
³ Mosling: Ann. Chem. (Liebig), 118, 303.

⁴ Green: Bull. Soc. Chim., 33, 426.

acid. The formation of symmetrical esters by the action of sodium ethylate upon the low-melting chloride also seems to furnish an argument against this explanation.

II. The Action of Alcohols and Alcoholates on the Chlorides.

The action of alcohols upon the chlorides has been previously studied in this laboratory,¹ as well as elsewhere,² and it has been shown that the first products formed are ester chlorides which, upon further action of the alcohol, are transformed into the ester acids:



With the low-melting chloride the ester chloride is easily formed, while its isomer is only slowly attacked by cold alcohol.

The work along this line was continued by R. M. Bird,³ who studied the action of the alcoholates as well. A brief summary of his results is as follows: The low-melting chloride, when dissolved in cold methyl alcohol, passed into the orthosulphone chloride and methyl benzoate. Upon evapora-

¹ Remsen and Dohme; *THIS JOURNAL*, **11**, 341. Remsen and Karslake: *Ibid.*, **18**, 825.

² List and Stein: *Ber. d. chem. Ges.*, **31**, 1659.

³ *THIS JOURNAL*, **30**, 247.

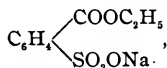
ting the solution the substance separated in small, diamond-shaped crystals which melted at 57° – 58° (corr.). They were soluble in alcohol and ether, but insoluble in water. Cold dilute sodium hydroxide did not affect the substance, but upon boiling it dissolved and chlorine was removed.

When the low-melting chloride was dissolved in methyl alcohol and the alcohol immediately boiled off, the orthosulphonic acid of methyl benzoate was obtained. Another product of this reaction was an oil which was shown to contain chlorine, and to it was assigned the formula of the orthosulphone chloride of methyl benzoate above described. It is, however, not stated that the oil became crystalline.

The orthosulphone chloride of ethyl benzoate was obtained by treating the dry, low-melting chloride with an alcoholic solution of sodium ethylate, until no more sodium chloride was precipitated. Upon extraction with ether and evaporation of the solvents, an oil remained which was insoluble in water, but soluble in alcohol and ether. When boiled with water it was hydrolyzed to an acid and hydrochloric acid was liberated. Treatment with ammonia yielded the orthosulphone amide of ethyl benzoate.

What was, apparently, the same oil was obtained by treating an alcoholic solution of sodium ethylate with an ethereal solution of the low-melting chloride. As a by-product of this reaction another oil was obtained which answered the description of the diethyl ester of orthosulphobenzoic acid obtained by Remsen and Dohme.¹ It was soluble in water, alcohol and ether, and contained no chlorine.

By this same treatment and 2 hours' standing before examining the products, the sodium salt of the formula,



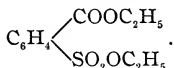
was formed.

A slightly warm solution of 1.070 grams of sodium ethylate, in absolute alcohol, was gradually added to 1.996 grams of the low-melting chloride, in ethereal solution. The reaction pro-

¹ THIS JOURNAL, 11, 332.

gressed until one-half of the ethylate had been added, when it suddenly stopped and could be induced to go no further. The resulting product was an oil. With dry ammonia, crystals were produced which melted at 225° – 226° . They were acid toward litmus and potassium carbonate. The crystals gave a product with a sweet taste when boiled with concentrated ammonia, as also did the oil when treated in the same manner. Upon boiling the oil with water it was hydrolyzed to an acid. No formula was assigned to the substance.

An excess of ethyl alcohol was added to the low-melting chloride and boiled for 35 minutes. There resulted nothing but a neutral oil, which was soluble in water, alcohol and ether; it contained no chlorine. Upon boiling with sodium hydroxide, ethyl alcohol was formed. The formula assigned was that of the diethyl ester,



None of the compounds above described, with the exception of the orthosulphone chloride of methyl benzoate and the sodium salt of ethyl orthosulphobenzoate, were analyzed. Certain considerations made it seem well to repeat the work :

1. The formation of ester chlorides by the action of sodium ethylate on the chlorides, and the impossibility of causing the reaction to go further.
2. The solubility of the so-called diethyl esters in water.
3. The production of a substance of acid reaction by boiling with ammonia.
4. The impossibility of obtaining the ester of a sulphonic acid by boiling its chloride with alcohol. Sulphonic acid esters are saponified by this process.

Action of Methyl Alcohol on the Low-Melting Chloride.—Ten grams of the low-melting chloride were dissolved in 30 or 40 cc. of cold methyl alcohol, and the solution allowed to stand 2 hours. At the end of that time the alcohol was evaporated by warming the solution and drawing air through it. When the proper concentration had been reached, very small, diamond-

shaped crystals separated from the solution. The evaporation was continued until no more crystals deposited, when they were filtered off and washed with water to remove the alcohol and hydrochloric acid which is formed in the reaction. The substance agreed in most of its properties with that prepared by Bird. It is soluble in alcohol and ether, but insoluble in water. Cold alkali, whether concentrated or dilute, has no effect upon the compound, but on boiling it dissolves and chlorine is removed. The melting-point, 63° – 64° (uncorr.), is rather higher than that given by Bird, but it is probable that his material was somewhat impure, since his figures differ considerably from the calculated values.

Analysis¹:

0.1062 gram substance gave 0.1592 gram CO_2 and 0.0276 gram H_2O .

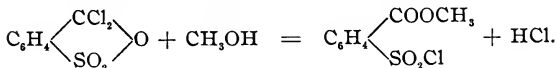
0.2354 gram substance gave 0.2401 gram BaSO_4 (Carius).

To determine the chlorine the substance was saponified by heating with pure sodium hydroxide and titrated to neutrality with nitric acid. The chlorine was then determined with a 0.1 N solution of silver nitrate. Sodium chromate was used as the indicator:

0.1835 gram substance required 7.8 cc. 0.1 N AgNO_3 .

	Calculated for $\text{C}_6\text{H}_4\begin{matrix} \text{COOCH}_3 \\ \text{SO}_2\text{Cl} \end{matrix}$	Found.
C	40.90	40.88
H	3.01	2.92
Cl	15.11	15.06
S	13.66	14.00

The reaction is to be expressed as follows:



The action of boiling ethyl and methyl alcohols has been fully investigated by former workers.² The reaction with

¹ The method employed for the determination of carbon and hydrogen was that described by Morse and Taylor: *THIS JOURNAL*, 33, 591. See also L. S. Taylor, Dissertation, J. H. U., 1905.

² Remsen and Dohme: *THIS JOURNAL*, 11, 341. Remsen and Karslake: *Ibid.*, 18, 825.

methyl alcohol was repeated and the product was found to be the ester acid. No trace of the oil containing chlorine, as described by Bird, was obtained. The analogous reactions with ethyl alcohol have already been given.

Action of Methyl Alcohol on the High-Melting Chloride.—On the high-melting chloride the alcohols, in general, react with less ease than upon the low-melting chloride. Upon boiling, however, the ester acids are also produced.

By boiling either chloride with 95 per cent ethyl alcohol for some hours, Bird obtained an acid of which the barium salt contained from 28 to 29.5 per cent of barium. Humphreys¹ had already obtained the same acid by boiling the orthosulphone chloride of phenyl benzoate for 12 hours, in absolute alcohol.

In the course of the present investigation the reaction described by Bird was repeated, with the hope of obtaining some light on the composition of this acid. Five grams of the high-melting chloride were boiled for 13 hours with absolute ethyl alcohol. The formation of ethyl chloride was continuous. After the reaction was over the alcohol was distilled off, and the remaining hydrochloric acid was expelled by heating on the water-bath. The product was dissolved in water, filtered from the small insoluble residue and boiled with barium carbonate until no more was dissolved. After crystallization the salt was dried and analyzed for barium; 0.1800 gram of substance gave 0.868 gram BaSO_4 . Found: Ba, 28.37 per cent. This was evidently the same acid that had been obtained by Humphreys and Bird. Since no formula could be assigned to the substance from the analysis of its barium salt, an effort was made to learn its structure in another way. The experiment was repeated with an equal quantity of the chloride and the barium salt prepared as before. This was converted into the sodium salt and, after evaporating to dryness, the salt was treated with phosphorus pentachloride. Reaction took place immediately. After heating some time to expel the oxychloride, water and ice were added and the material was ground until all traces of the oxychloride had been removed.

¹ Dissertation, J. H. U., 1900.

After washing several times with water, strong ammonia was added and the mixture was warmed on the water-bath. The solutions became sweet and, with hydrochloric acid, gave a heavy precipitate of saccharin. This experiment pointed to the presence of orthosulphobenzoic acid. The following considerations lead to the same conclusion: The action of boiling alcohol on the chlorides is known to produce the ester acid. Further action of the alcohol yielded the unidentified acid. The action of alcohol on the phenyl ester chloride must first convert it into the ester acid. Upon further boiling, the unidentified acid was also formed. These facts show that a change in the carboxyl group must have taken place. The action of phosphorus pentachloride, already referred to, showed the acid to be dibasic. The ethyl esters of carboxyl acids are not saponified by absolute alcohol, however, and a special reason must be sought in this case. It has been stated that ethyl chloride was formed constantly and for every molecule of ethyl chloride 1 molecule of water must have resulted. The tendency of the water should be to saponify the ester and there would result an equilibrium between orthosulphobenzoic acid and the ester acid. In the experiments performed by Bird he obtained the acid after boiling with 95 per cent alcohol for 3 hours, while in the experiments last described it was necessary to heat with absolute alcohol for 13 hours. Providing that all of the hydrochloric acid formed in this reaction reacted with the alcohol, then, for every molecule of chloride used, enough water would be formed to saponify 2 molecules of the ester acid. The presence of the alcohol would cause an equilibrium to exist between the ester acid and orthosulphobenzoic acid. It appears, therefore, that the salt containing about 28 per cent barium is probably a mixture of a salt of orthosulphobenzoic acid and a salt of the ester acid.

III. Action of Sodium Ethylate on the Chlorides.

High-Melting Chloride.—Five grams of the high-melting chloride were dissolved in dry ether and an alcoholic solution of sodium ethylate was gradually added until the reaction ceased. The experiment is best carried out in a bottle, which

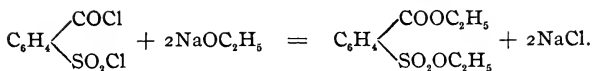
may be corked and well shaken from time to time, because the precipitated sodium chloride is voluminous and interferes with the reaction. In no case were less than 2 molecules of ethylate required. The action never stopped half way, and the addition of an excess of ethylate was often found necessary in order that the reaction might be complete. After the action was over, the resulting mixture was poured into a separating-funnel containing acidulated water. The contents were thoroughly shaken until the sodium chloride and excess of ethylate were dissolved, when the aqueous layer was run off. The ethereal layer was washed several times with water, then removed and dried over calcium chloride for 12 hours. After filtration and evaporation of the ether an oil remained which was soluble in alcohol and ether, but insoluble in water. It was neutral to litmus. Various methods for its purification were tried, but none was successful until distillation under reduced pressure was employed. Analysis :

0.1540 gram substance gave 0.2899 gram CO_2 and 0.0738 gram H_2O .

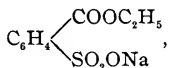
0.3493 gram substance gave 0.3243 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OC}_2\text{H}_5 \end{cases}$	Found.
C	51.12	51.33
H	5.47	5.37
S	12.41	12.74

These values point conclusively to the formula of the diethyl ester. It boils at $212^\circ\text{--}213^\circ$ (21 mm.). At this pressure the ester distils with very little decomposition. It should be allowed to stand after distillation, for some hours, as a few crystals of sulphobenzoic anhydride usually separate. They can be removed by filtration. At a greater pressure, however, the ester distils with much decomposition. Among the products formed are sulphobenzoic anhydride and ethyl benzoate. The former was identified by its melting point ($129^\circ.5$), and by its conversion into sulphonefluorescein when fused with resorcinol. The ethyl benzoate was detected by its odor. The reaction is expressed by the equation :



The yield of ester by this method was always small. The fact, established by Bird, that when the mass is allowed to stand a salt of the formula,



is formed, suggested the explanation of the small yield. The alcohol used as the solvent for the ethylate would tend to saponify the ester, and the acid thus formed would be converted into its sodium salt by the action of the ethylate. To test this point the experiment was repeated as above, except that no alcohol was used, the ethylate being added in the dry state to the ethereal solution of the chloride. The yield of ester was almost theoretical. No sulphone chloride was obtained in the experiments.

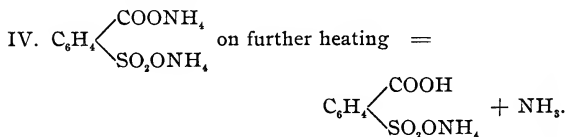
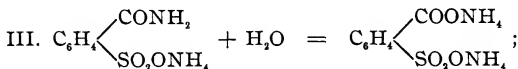
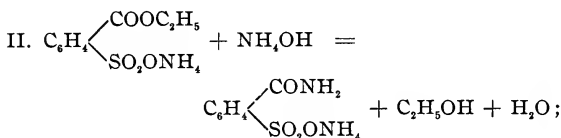
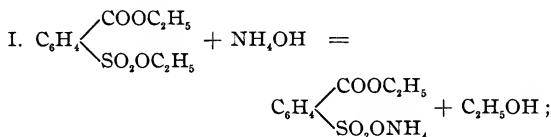
Upon boiling the impure ester with ammonia a sweet compound was usually produced, and sometimes a precipitate of saccharin appeared upon acidification. No such reaction takes place with the pure ester, however. Furthermore, the impure ester always gives a test for chlorine, while the pure substance is entirely free from it. These facts show that a small quantity of unchanged chloride is usually present in the impure ester. They also tend to explain certain observations made by Bird, which have already been referred to.

It is a fact that the action of ammonia upon the ester produces a substance which has an acid reaction. The ester is boiled, with frequent additions of concentrated ammonia, until it dissolves. This operation requires half an hour or longer. The solution is then evaporated to the proper concentration and allowed to cool. If the ammonia gas has all been expelled from the solution, the acid ammonium salt of orthosulphobenzoic acid separates. A determination of the nitrogen in the salt showed this to be the case.

0.1097 gram substance gave 0.006858 gram N (absolute).

	Calculated for	
	$\text{C}_6\text{H}_4 \begin{cases} \text{COOH} \\ \text{SO}_2\text{ONH}_4 \end{cases}$	Found.
N	6.40	6.25

In order to obtain confirmatory evidence, if possible, a quantity of the acid ammonium salt of orthosulphobenzoic acid, which had been made by the hydrolysis of saccharin, was dissolved in an excess of strong ammonia and the solution evaporated. After the odor of ammonia had disappeared the solution was found to have become acid and crystals of the acid ammonium salt were obtained upon further evaporation. Ammonium sulphobenzoate was found to behave in the same way. The reactions must be expressed as follows :



With saponifying agents, the first point of attack is the sulphonic acid group. With aqueous alkali the ester is only slowly changed owing to its insolubility in water, but when alcoholic alkali is employed the reaction proceeds with ease. The final product of the action of alkalis is the neutral salt of

orthosulphobenzoic acid. Aqueous ammonia acts more easily than aqueous alkali.

Low-Melting Chloride.—The action of sodium ethylate on the low-melting chloride also results in the formation of the diethyl ester. The ester agrees in all its properties with the one prepared from the high-melting chloride. Analysis :

0.1537 gram substance gave 0.2863 gram CO_2 and 0.0794 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OC}_2\text{H}_5 \end{cases}$	Found.
C	51.12	51.46
H	5.47	5.86

The reaction was tried under various conditions, an alcoholic solution of sodium ethylate was added to the dry chloride ; the chloride, in ether, was treated with an alcoholic solution of the ethylate, and, finally, dry ethylate was added to an ethereal solution of the chloride. The last was found to be the most satisfactory method.

The neutral oils soluble in water, which are described by Bird, have not been obtained.

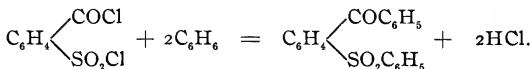
On grinding together dry sodium ethylate and dry, low-melting chloride, Bird obtained a product that he was not able to identify. The reaction is explosive and difficult to control. Furthermore, more or less decomposition takes place. On repeating the reaction the substances were mixed, in very small portions, in a large test-tube and stirred with a glass rod. After the reaction, water and ether were added and the tube was shaken. The ether was found to contain a little oil in a very impure state and in quantity insufficient for distillation. It was neutral and insoluble in water, however, and there seems to be no reason for doubting that it was the diethyl ether.

IV. Action of Benzene and Aluminium Chloride.

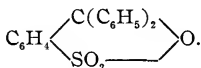
The action of benzene on the chlorides, in the presence of aluminium chloride, was first studied by Remsen and Saunders.¹

¹ THIS JOURNAL, 17, 347.

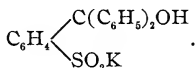
They showed that the high-melting chloride reacts to form, as the final product, orthobenzoyldiphenylsulphone, as follows :



This substance melts at 183° – 184° . In studying the reaction with a mixture of the two chlorides, by far the largest portion of the product was the same substance. They obtained simultaneously, however, another compound, melting at 162° – 163° . Analysis showed it to be of the same empirical formula as the first one, but its conduct, when fused with potassium hydroxide, led them to assign to it the formula of the lactone,



In their article upon the chlorides of orthosulphobenzoic acid, List and Stein¹ also describe the substance. They obtained it by the action of benzene and aluminium chloride upon the mixed chlorides. The reaction was allowed to proceed at the ordinary temperature for some days, after which the mixture was warmed for a time. The substance dissolved in boiling, alcoholic potassium hydroxide with the formation of a potassium salt of the formula



Upon treatment with acids the lactone was recovered.

Since it has been possible to isolate the low-melting chloride in a pure condition, many attempts have been made to prepare this substance. None of them has been successful, the sole product of the reaction being always the symmetrical compound, orthobenzoyldiphenylsulphone, identical with that derived from the high-melting chloride.

The writer made several attempts to obtain the lactone by the action of benzene and aluminium chloride upon the low-

¹ Ber. d. chem. Ges., 31, 1648.

melting chloride, but always without success. The reaction was allowed to take place at the room temperature, during a period of 3 or 4 days, and also at the temperature of a boiling water-bath, when it is complete in a short time. Finally, a mixture of 60 per cent of the low-melting chloride and 40 per cent of the high-melting chloride was dissolved in pure, dry benzene, and aluminium chloride was added from time to time. The reaction was allowed to proceed at the room temperature. The resulting product was found to be symmetrical however, no trace of the lactone being formed. The proportion of the two chlorides taken is about that in which they occur in the mixture which is obtained by the action of phosphorus pentachloride on the acid potassium salt. It was with this mixture that List and Stein obtained their results.

From the experiments of former workers, as well as from those last recorded, it would seem doubtful if the product first described by Remsen and Saunders, and later by List and Stein, was in reality the lactone as supposed. A substance has been obtained by another method, however, and will be described presently, which analysis shows to be the lactone and which, moreover, agrees with the description of the lactone made as above. Such being the case, the conclusion must be that the action of benzene and aluminium chloride has, in two instances at least, given the lactone. From the failure of other workers to obtain it, it is evident that peculiar conditions must be necessary to its formation.

V. Experiments with Thionyl Chloride.

Since the methods which are employed for the preparation of the chlorides, especially in the case of the low-melting one, fail to give satisfactory yields, it seemed desirable to try the action of thionyl chloride on both the acid and neutral salts, in the hope that this reagent might give better results than the pentachloride or oxychloride of phosphorus.

Ten grams of the dried and finely pulverized neutral potassium salt of orthosulphobenzoic acid were placed in a small balloon flask, and an equal weight (2.5 mol.) of thionyl chloride was added. The flask was fitted to a return condenser, which was provided

at its upper end with a Peligot tube containing a strong solution of sodium hydroxide, to absorb the sulphur dioxide which was given off. The reaction started without the application of heat, but did not become vigorous. At the temperature of the boiling water-bath, however, it progressed rapidly. The heating was continued until no more sulphur dioxide was liberated, about 45 minutes being required. During the progress of the reaction the mass became more and more viscous, until at the end the appearance had become like that of thick starch paste. The condenser was then reversed and the excess of thionyl chloride was distilled off. This process was much facilitated by slightly diminishing the pressure. After the removal of the excess of thionyl chloride, the mass became crystalline. It was removed from the flask and ground in a mortar with water containing ice, and then poured into a separating funnel and shaken with ice-water and ether. A portion of the material did not immediately go into solution but dissolved gradually, as the shaking was continued. After removing the ethereal layer it was examined with the expectation of finding one or both of the chlorides of orthosulphobenzoic acid. All that was obtained, however, was a small quantity of the anhydride of orthosulphobenzoic acid which had escaped hydrolysis in the treatment with water. A portion of this material, which did not dissolve readily, was filtered off and examined. It was found to contain potassium and chlorine, and to show an acid reaction with litmus. On boiling with water it was dissolved and hydrochloric acid was formed. A small quantity was dried on a porous plate and placed in a desiccator over sulphuric acid. It was hoped in this way to obtain a specimen for analysis in fairly pure condition, but upon opening the desiccator, some hours later, fumes of hydrochloric acid escaped, showing that the substance had been hydrolyzed. No further effort was made to obtain the pure compound, but its composition was shown by another method.

The reaction between the neutral salt and thionyl chloride was repeated in the manner above described, but after distilling off the excess of the latter, absolute alcohol was added and the mixture boiled. At the end of an hour the alcohol was

filtered off. Upon cooling, crystals separated in the form of thin leaves, these were removed and analyzed for potassium :

0.1050 gram substance gave 0.334 gram K_2SO_4 .

	Calculated for $C_6H_4 \begin{matrix} \swarrow COOC_2H_5 \\ \searrow SO_2OK \end{matrix}$	Found.
K	14.59	14.28

The yield of these crystals was only about 0.5 gram, showing that the reaction had, for the most part, progressed beyond the first stage. That even a small quantity of this salt was obtained, however, points conclusively to the presence of a

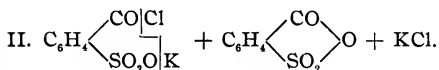
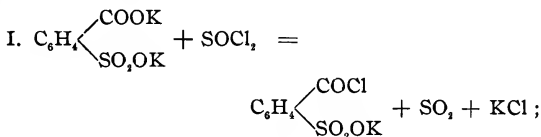
compound of the formula $C_6H_4 \begin{matrix} \swarrow COCl \\ \searrow SO_2OK \end{matrix}$. That the structure

of this monochlorinated derivative of the neutral potassium salt is that which has been assigned to it, rather than that of the

isomeric sulphone chloride, $C_6H_4 \begin{matrix} \swarrow COOK \\ \searrow SO_2Cl \end{matrix}$, is evident from the

fact that it is converted into an ester upon boiling with alcohol, a reaction which does not occur with the sulphone chlorides.

The formation of the anhydride, then, takes place in two stages, the first product being a monochlorinated derivative which passes into the anhydride by loss of potassium chloride :



The next experiment was performed with the intention of determining whether or not the anhydride could profitably be prepared by this method. Thirty-four grams of the neutral

potassium salt were treated with a large excess (5 or 6 mols.) of thionyl chloride and heated on the water-bath until no more sulphur dioxide escaped. About one hour was required. The excess of thionyl chloride was then distilled off and the residue in the flask was extracted with dry benzene. Only 7 grams (31 per cent) of the anhydride were obtained, however. It is probable that if the heating had been allowed to proceed longer, the yield would have been larger, but the experiment was not repeated with the neutral salt, since the acid salt was found to give much more satisfactory results.

The final experiment with the neutral salt was an attempt to prepare a chloride of orthosulphobenzoic acid. Twenty grams of thionyl chloride were poured into a Carius tube, an equal weight of the neutral salt added and a thorough mixture made. After heating at 125° , for 13 hours, the tube was opened and found to contain anhydride, but no chloride was present. In order to isolate the chloride, if formed, the reaction mixture was shaken with water, ice and ether. Since the greater part of the anhydride was hydrolyzed by this process, the quantity formed was not determined.

Experiments with the Acid Salt.—Both the neutral and acid potassium salts of orthosulphobenzoic acid are attacked with about the same ease by thionyl chloride. With the acid salt the reaction takes place with the formation of hydrochloric acid, showing that the point of attack is the carboxyl. With the acid salt, as with the neutral, no chloride was obtained either under the ordinary pressure or in a sealed tube. As a method of preparing the anhydride, however, the action of thionyl chloride was found to be very satisfactory. Two experiments were conducted; in the first, 10 grams of the acid salt were heated on the water-bath with a large excess of thionyl chloride. The reaction was complete in 45 minutes. After distilling off the excess of thionyl chloride, the residue was extracted with dry benzene. Four grams of the anhydride were obtained, which corresponds to a yield of 52 per cent.

The second experiment was conducted with somewhat larger quantities. Twenty-seven grams of the acid salt were heated

on the water-bath with 56 grams of thionyl chloride. The volatile reaction products ceased to escape in about an hour, but the mixture was heated for 1.5 hours longer, and was then treated in the usual way. Sixteen and five-tenths grams (80 per cent) of the anhydride were obtained.

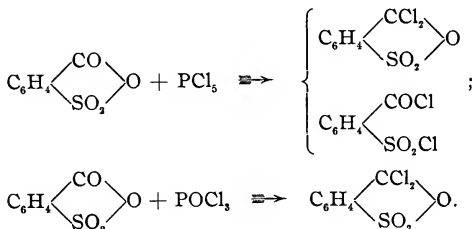
In order to get the best results, it has been found advisable to use a large excess of thionyl chloride, by so doing the mixture remains in a semi-liquid state, and better contact is secured. It is also advisable to heat for an hour or two after the volatile reaction products have ceased to escape. The thionyl chloride recovered is quite pure and may be used again.

The results of these experiments indicate that the normal reaction of chlorinating agents on both the acid and neutral salts is the formation of a monochlorinated derivative containing the chlorine in combination with the carbonyl. This passes into the anhydride by the loss of potassium chloride. The formation of the two dichlorides of orthosulphobenzoic acid remains to be explained. In the preparation of the high-melting chloride, about 60 per cent of the low-melting chloride is also produced. When the neutral salt is treated in the same manner a mixture is also obtained. In this case the chlorinating agent is phosphorus pentachloride. On the other hand, in the preparation of the low-melting chloride by the action of phosphorus oxychloride on the neutral salt, practically none of the high-melting chloride is formed. The formation of the high-melting chloride, then, is favored by the action of a powerful chlorinating agent.

List and Stein¹ have shown that the action of phosphorus pentachloride on the anhydride, at high temperatures, gives rise to the formation of both chlorides. For the sake of comparison, the action of the oxychloride upon the anhydride was tried. Twelve grams of the anhydride were heated for 14 hours with phosphorus oxychloride, at 125°. At the end of that time the mixture was examined and it was found that, while the reaction was by no means complete, about 2 grams of the low-melting chloride had been formed. It was identi-

¹ Ber. d. chem. Ges., 31, 1659.

fied by its melting point. In order to test for the presence of high-melting chloride, ammonia was added but no sweet taste was produced. The action of phosphorus pentachloride probably takes place as follows: The anhydride is first formed and it is attacked in two ways by the pentachloride, with the formation of two isomeric substances. The action of the oxychloride can take place in only one way, however, since only one product is formed. If the action of the oxychloride were not considered, one might assume that with the pentachloride the reaction all goes in one direction, and that a rearrangement takes place. The fact that neither chloride can be changed into the other by heat, also argues against the latter supposition. The pentachloride, then, must have the power to chlorinate both the carbonyl group of the anhydride and also to replace the anhydride oxygen atom. It would be expected that the latter reaction would take place with the greater difficulty and, as already stated, the yield of high-melting chloride, when prepared from the acid salt, is only 40 per cent of the total. The oxychloride can only attack the carbonyl group, while, as has been shown, thionyl chloride does not react with the anhydride:



VI. Experiments with Magnesiumphenyl Bromide.

Action on the High-Melting Chloride.—With the high-melting chloride magnesiumphenyl bromide reacts only at the boiling point of ether, while with the low-melting chloride the reaction is so violent that the solutions must be cooled with ice and mixed very slowly. The resulting products are very difficult to purify. In the case of the high-melting chloride the product

has been fully identified, while with the low-melting chloride satisfactory results have not been obtained.

Ten grams of the high-melting chloride were dissolved in dry ether, and to the solution an ethereal solution of 3.5 molecules of magnesiumphenyl bromide was added. The mixture was boiled for an hour or two until the oily substance which settled to the bottom of the flask did not increase in quantity. At this point the ether above the oil had become clear. The ether was then poured off and the residue in the flask was shaken with water and dilute hydrochloric acid. After the decomposition had been effected, the resulting oil was allowed to settle and the water and acid were poured off. It was washed with several changes of water. Steam was then conducted into the flask to remove any brombenzene which might have been present. After many unsuccessful attempts to purify this oil, the following method was found satisfactory: The oil was allowed to stand under water for a week or more. At the end of this time it had usually solidified, for the most part. It was then heated to boiling with methyl alcohol and the alcohol poured off while still hot. This treatment removed the un-solidified portion. The solid remaining was then crystallized from ethyl alcohol. The oil is easily soluble in alcohol and ether. After solidification, however, it is soluble in these liquids with much greater difficulty.

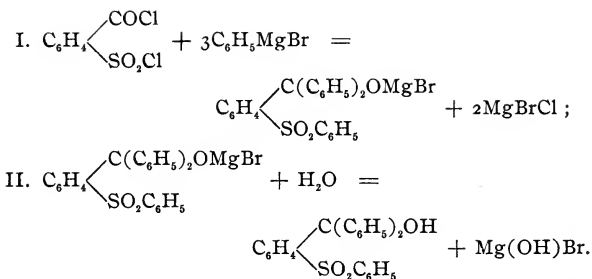
The product which had been crystallized from alcohol melted at 183° – 184° . It is not affected by alcoholic potassium hydroxide. With concentrated nitric and sulphuric acids a dark red color is produced, an indication of the carbinol condition. Analysis:

0.1284 gram substance gave 0.3509 gram CO_2 and 0.0603 gram H_2O .

0.2146 gram substance gave 0.1268 gram BaSO_4 (Carius).

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{C}(\text{C}_6\text{H}_5)_2\text{OH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{cases}$	Found.
C	74.95	74.52
H	5.04	5.26
S	8.00	8.11

The reaction must be represented as follows:

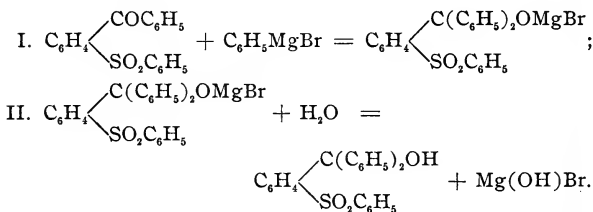


The structure of this substance was established by treating orthobenzoyldiphenylsulphone with magnesiumphenyl bromide. The product thus obtained melted at the same temperature, and the melting point of a mixture of the two preparations remained unchanged. Analysis :

0.1378 gram substance gave 0.3783 gram CO_2 and 0.0661 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{C}(\text{C}_6\text{H}_5)_2\text{OH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{cases}$	Found.
C	74.95	74.86
H	5.04	5.37

The reaction is represented by the equations :



Action on Sulphobenzoic Anhydride.—The reaction of magnesiumphenyl bromide on sulphobenzoic anhydride was tried, in the hope of obtaining a diphenylated derivative. This product was obtained and has been referred to under the reaction of benzene and aluminium chloride. The action is

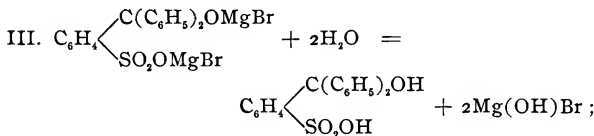
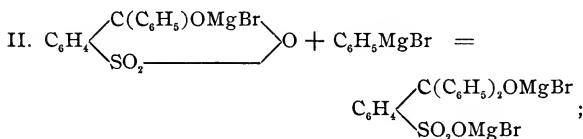
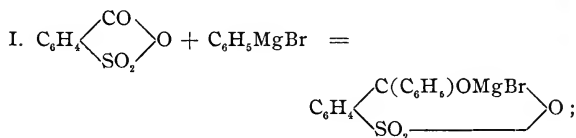
vigorous, and the solutions should be cooled with ice. After standing some time, water and sulphuric acid were added and the contents of the flask were well shaken with ether. Upon examination of the ethereal layer a product was obtained which, when crystallized from alcohol, melted sharply at 163° (uncorr.). It dissolved in alcoholic potassium hydroxide, on boiling, with the formation of a salt soluble in water. Upon acidification the original substance was precipitated. Neither water nor aqueous potassium hydroxide would dissolve the substance even when boiled. Analysis :

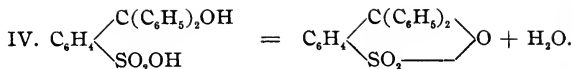
0.1070 gram substance gave 0.2772 gram CO_2 and 0.0447 gram H_2O .

0.2056 gram substance gave 0.1564 gram BaSO_4 (Carius).

	Calculated for $\text{C}_6\text{H}_4\left\langle \begin{array}{c} \text{C}(\text{C}_6\text{H}_5)_2 \\ \text{SO}_2 \end{array} \right\rangle \text{O}$.	Found.
C	70.76	70.64
H	4.38	4.68
S	9.95	10.40

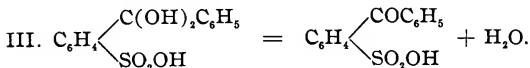
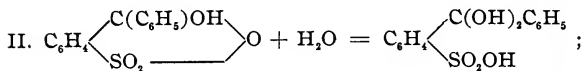
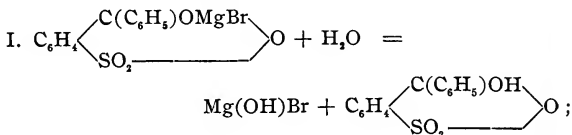
The reaction may be expressed as follows :





The substance just described is formed to the extent of only about 10 per cent. It is probable that the reaction, in the main, stops at stage I. The product would then be hydrolyzed

to form the acid, $\text{C}_6\text{H}_4 \begin{array}{l} \text{COC}_6\text{H}_5 \\ \text{SO}_2\text{OH} \end{array}$, as follows :



This compound is not of any special interest and no attempt was made to separate it. Since the substance is soluble in water, it did not appear in the ethereal extract of the products.

JOHNS HOPKINS UNIVERSITY.

NOTE ON "THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES."

BY ROGER CLARK WELLS.

In the article by me in the February number of this JOURNAL, there was, I regret to state, an incorrect conclusion. In trying to estimate the magnitude of possible error upon the determination of the atomic weight of sodium due to time effects in nephelometry, I based my reasoning upon the behavior of intense opalescences, whereas, really, only weak opalescences were concerned. Professor Richards, to whom I had, unfortunately, not presented the paper for preliminary reading, im-

mediately called my attention to this and I am very glad to correct it. It results, therefore, that the correction, if any, must be even less than 0.001 of a unit in the atomic weight of sodium and, hence, quite negligible.

Lest some may attach too much significance to the times of maximum opalescences, I wish to emphasize the fact that the opalescences, especially weak ones, are changing very slowly just before and after their maxima, so that the exact time to a minute means little. Moreover, the variation is occasionally large. The anomalous results illustrating this, referred to in the foot-note on p. 111, were probably due to an insufficient excess of precipitant. Previous work had shown that a long time was often necessary for the opalescences to become relatively stable. My experiments were made to discover the means by which to obtain the maximum opalescence as speedily as possible, and showed that, under the conditions mentioned, on the average, intense opalescences become relatively stable in from 1 to 20 minutes, medium opalescences in from 10 to 40 minutes and weak opalescences in 30 minutes or over.

The maximum was chosen as the best measure of the opalescence, and it could always be found by comparing the opalescence at any time with an unchangeable ground glass. In consequence of the time effects above noted, such a method is more necessary for intense opalescences, which change quickly, than for weak ones which change very slowly. In the case of weak opalescences, the older procedure of waiting a long time before reading, two tubes would yield almost precisely the same result as reading each at its maximum.

In brief, then, as far as time effects in nephelometry are concerned, the time factor must be carefully regulated for intense opalescences, but it ceases to be a major variable with weak ones.

Contribution from the Chemical Laboratory of Harvard College.

NOTE CONCERNING THE USE OF THE NEPHELOMETER.

BY THEODORE WILLIAM RICHARDS.

A recent article by Dr. R. C. Wells upon "The Estimation of Opalescent Silver Chloride Precipitates" with the help of the nephelometer¹ seems to call for a few additional remarks. The following note is written in order to supplement his suggestions, and to point out clearly the range of applicability of nephelometric methods.

Dr. Wells' conclusions are based upon a series of comparisons in which the cloudiness of a ground glass plate was used as the standard of comparison with the cloudiness produced by opalescent precipitates. This is a good idea, but it is evident that the intensity of light reflected to the eye-piece from this plate will vary with the inclination of the plate to the source of light and, therefore, that great care must be taken to have this inclination always definite. Undoubtedly, this was taken into account, but the necessity of this precaution was not sufficiently emphasized.

Another cause of uncertainty which, although mentioned as a possible source of error, and also heeded to some extent, may not have been quite sufficiently guarded against in the experimental work, is variation in temperature. Silver chloride is much more soluble in hot than in cold water, and the form of aggregation of the precipitate varies greatly with the temperature. Both these facts cannot but affect the rate of formation of the opalescent precipitate; hence, any work aiming at definite comparison with a fixed standard should be conducted in thermostatted tubes.

Qualitatively, it has been known for many years that the rate of decay of the opalescence, as well as the rate of precipitation, varies greatly with the "concentration" of the precipitate, in other words, with the weight of precipitate suspended in a given volume of liquid. An intense opalescence settles

¹ THIS JOURNAL, 35, 99 (1906).

out much more quickly than a faint one. Dr. Wells has quantitatively estimated this difference of behavior. A saturated solution of silver chloride, such as is usually studied by means of the nephelometer, ordinarily contains not much over 1.5 milligrams per liter, or is only about 0.00001 N; but two-thirds of the figures given by Dr. Wells refer to solutions as strong as 0.00004 N, nearly four times as concentrated. While it is a matter of great interest to study, as Dr. Wells has done, the rapid rate of deposition of these more concentrated opalescences, they should probably not be made the basis of exact quantitative analytical work, because of their rapid rate of change. For quantitative estimation of the substance in such mixtures, it is better not to use the nephelometer, but to collect the precipitate after it has been wholly deposited. The nephelometer should be employed for exact work only when the precipitate is so finely divided that it will not in any reasonable time, for example 2 or 3 days, deposit itself and thus place itself within the range of ordinary quantitative determination.

It should be strongly emphasized that the "anomalous results" mentioned by Dr. Wells had been duly considered in previous work, and were distinctly pointed out, but the bulk of the previous papers was concerned with indicating the way in which the difficulties can be overcome; therefore but few figures were given.

While the ground glass plate employed by Dr. Wells, when properly and steadily illuminated, undoubtedly affords an excellent means of studying the rate of change in a given mixture, I cannot believe that it provides the best standard of reference for analytical purposes, because it is unaffected by the many variables which affect the mixture to be estimated. In my opinion, if even moderately accurate analytical results are to be had with the nephelometer, the one essential point to be heeded is this: *the unknown solutions to be estimated must be treated in exactly the same way as the known standard solutions, which serve as the basis of comparison.* If this precaution is adhered to, the changes of temperature, the presence of electrolytes, the concentration of the solutions and all the other

variables, affecting each precipitate in like manner, are eliminated from the comparison. This method, indeed, is a fundamental principle in all precise volumetric analysis.

That this precaution was realized in the previous discussion of the instrument may be shown by the following quotation :

"Care must be taken to have both standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use."

"The contents of this paper may be summarized as follows : The chief possibility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way."¹

On the same page with these statements is to be found a series of results showing, positively, that when this advice is heeded, and when sufficient time is allowed for the opalescence to develop, the instrument gives reasonably accurate results, and similar evidence is given in another place.

In the course of the work upon the atomic weight of sodium, a singular anomaly was observed, namely, the fact that the opalescence of silver chloride forms more quickly when a solution of this salt is treated with a large excess of silver nitrate than it does when an equivalent solution of sodium chloride is treated in the same way. This irregularity leads to an uncertainty as to whether the *weights* of precipitate corresponding to a given maximum intensity of opalescence are equal in the two cases—an uncertainty clearly pointed out in the place mentioned. The question of weight is not discussed in Dr. Wells' paper, but is now being exhaustively studied at Harvard. The uncertainty arose only because of a slight infringement of the rule italicized above. When the two mixtures are subjected to the same conditions—for example, when both are redissolved in ammonia and reprecipitated, the uncertainty dis-

¹ Richards and Wells : *THIS JOURNAL*, 31, 242 (1904). It should be noted that both these sentences were written by the author, who takes all the responsibility attached to them.

appears. This practice is being adopted in a research on the atomic weight of potassium, now being pursued at Harvard by Dr. A. Stähler, of Berlin, and the author.

In brief, the object of this note may be summarized as follows: It is pointed out that, while the recent paper of Dr. R. C. Wells on the nephelometer affords interesting data concerning the rate of precipitation of opalescent precipitates, particularly in cases verging upon prompt deposition, it does not emphasize the chief precaution which, in the author's opinion, should be adopted if the nephelometer is to be used in quantitative analytical work.

Contributions from the Chemical Laboratory of Harvard College.

ISOHEXANE AND A NEW DODECANE.

BY LATHAM CLARKE AND R. NORRIS SHREVE.

As the preparation of isohexane, according to Wurtz,¹ from isobutyl iodide, ethyl iodide and sodium, is unsatisfactory for the production of even moderately large quantities, a new method has been devised.

Methyl isobutyl ketone was obtained from ethyl isopropylacetacetate, and this, by reduction, was converted into methylisobutylcarbinol, which, by further reduction, yielded isohexane.

This procedure seems to be the best thus far devised for the production of isohexane, as the Wurtz method gives a very small yield, while the present one gives a yield of 57 per cent of the theoretical, reckoned from the carbinol, and about 37 per cent calculated from the ketone.

Incidentally, in the making of the carbinol, a small amount of pinacone was obtained, which was transformed into the corresponding dodecane, *viz.*, dimethyldiisobutylethane. Of the present series of hydrocarbons of established constitution, this, with the single exception of diisooctyl, is the first one above decane to be discovered which is not normal.²

¹ Jahresb. d. Chem., 1855, p. 574.

² Alechin: J. russ. Chem. Soc., 15, 175.

EXPERIMENTAL.

From ethyl acetacetate, ethyl isopropylacetacetate was prepared by Conrad's method,¹ from sodium ethyl acetacetate and isopropyl iodide. It boiled at 201°. The isopropyl iodide used was made by a modification of Markownikoff's method,² as follows: Two hundred grams of glycerin were mixed with 170 grams of water, 300 grams of iodine were added and, all at once, 60 grams of red phosphorus. The mixture was immersed in cold water for an hour, boiled with a return condenser over a free flame for 2 hours and distilled. The distillate was washed with water and with dilute sodium hydroxide solution, then with water again, and the colorless liquid dried with calcium chloride. On rectification it boiled at 89°. This method gave a consistent 70–80 per cent yield, reckoned from the glycerin.

Methyl Isobutyl Ketone.

This ketone has been prepared by Frankland and Duppa.³ We modified their method and prepared it from ethyl isopropylacetacetate, by boiling for 6 hours with 10 per cent potassium hydroxide solution, 2 mol. alkali : 1 mol. ester. The resulting mixture was distilled with steam. The oily layer floating on the distillate was separated, dried over calcium chloride and fractionated. The fraction boiling between 100°–130° was 4 times redistilled, until a portion boiling at 119° (765 mm.) was obtained. Wagner⁴ gives 115°.5 (745 mm.) and Frankland⁵ 114° (758 mm.). Two hundred and forty-five grams of ethyl isopropylacetacetate yielded 89 grams of methyl isobutyl ketone, corresponding to 55 per cent of the theoretical. In addition to the boiling point,⁵ the identity of this substance was further established by analysis.

I. 0.1052 gram substance gave 0.2790 gram CO₂ and 0.1043 gram H₂O.

¹ Conrad and Limpach: Ann. Chem. (Liebig), 192, 153.

² *Ibid.*, 138, 364.

³ Ann. Chem. (Liebig), 145, 82.

⁴ J. prakt. Chem., [2], 44, 281.

⁵ Ann. Chem. (Liebig), 145, 83.

II. 0.1805 gram substance gave 0.4735 gram CO_2 and 0.1974 gram H_2O .

	Calculated for $\text{C}_6\text{H}_{12}\text{O}$.	I.	Found.	II.
C	72.00	72.43		71.60
H	12.00	11.01		12.15

The substance is readily miscible with alcohol, ether, benzene, acetone and ethyl acetate, but is insoluble in water.

Methylisobutylcarbinol.

This carbinol has been made from isovaleraldehyde and zinc methyl by Kuwschinoff.¹ We obtained it from methyl isobutyl ketone in the following manner: Seventy-five grams of methyl isobutyl ketone were dissolved in 150 grams of ethyl ether and the solution poured over 125 grams of water, contained in a round-bottom flask with a return condenser attached. To the mixture was added, piece by piece, 38 grams of sodium, during a period of 3 hours. The ether layer was then decanted, washed with water to remove a white turbidity and fractionated. The residue from the ether yielded two fractions, one boiling at $100^\circ\text{--}150^\circ$, the other at $240^\circ\text{--}245^\circ$. The first was methylisobutylcarbinol, the second methylisobutylpinacene.

The first fraction was twice distilled and gave 53 grams of methylisobutylcarbinol, boiling at $138^\circ\text{--}145^\circ$, a yield of nearly 70 per cent of the theoretical. Analysis:

0.1540 gram substance gave 0.3959 gram CO_2 and 0.1853 gram H_2O .

	Calculated for $\text{C}_6\text{H}_{14}\text{O}$.	Found.
C	70.58	70.11
H	13.72	13.37

This compound has a peculiar odor like fusel oil. It is soluble in alcohol, ether, acetone, benzene, toluene, ethyl acetate and carbon tetrachloride; insoluble in water.

Ethylisobutyl.

This hexane has been prepared in the way already men-

¹ J. russ. Chem. Soc., 19, 205.

tioned by Wurtz,¹ and extracted from gasolin by Norton and Andrews.² We obtained it from methylisobutylcarbinol by the following procedure: Fifty grams of the carbinol were dissolved in 70 cc. of redistilled amyl alcohol (b. p. 115° – 125° , mostly near the lower figure) in a 500 cc. round-bottom flask, with a return condenser attached. Into this solution, cooled at 0° , was passed hydriodic acid gas, made from 88 grams of iodine,³ after which 150 grams of glacial acetic acid were added, together with several pieces of granulated zinc. The mixture was allowed to stand 4 days, zinc being once added to keep it always present in excess; at the end of this time it was heated over the free flame and a fraction distilled off between 60° and 95° . This fraction will be described later.

The residue from the distillation was treated with the hydriodic acid from 44 grams of iodine,⁴ and more zinc, after which the mixture was allowed to stand again for 4 days. The distillation was repeated under the same conditions as before, the residue being treated with the same amount of hydriodic acid. This process was carried through 5 times. The product of the first distillation weighed 10 grams. This, on rectification, gave 1–2 cc. of hydrocarbons, derived from the amyl alcohol, boiling between 35° and 40° ; 6 grams of isohexane, boiling at 64° , and a residue of amyl acetate and acetic acid. By the same treatment, the second distillate yielded 9 grams of rectified hexane; the third, 6.5 grams; the fourth, 7 grams; the fifth, 1.5 grams; and the sixth, 2.5 grams. The total yield of isohexane was 32.5 grams, but this contained nearly 3 per cent of iodine, although it boiled almost constantly at 62° – 64° . By shaking with concentrated sulphuric acid and distilling, the iodine was removed entirely and a yield of 24 grams of isohexane obtained, corresponding to 57 per cent of the theoretical.

The success of this method seems to depend on the following facts: In the first place, the large amount of high-boiling solvents—amyl alcohol, amyl acetate and acetic acid—holds in

¹ Jahresb. d. Chem., 1855, p. 574.

² THIS JOURNAL, 8, 6.

³ Gatterman: "Pract. Meth. Org. Chem.," 2d Am. ed., p. 345.

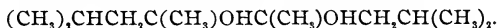
⁴ Gatterman: *Loc. cit.*

solution the low-boiling hexane, and thus keeps it from evaporating during the several days of standing while the reduction is taking place. Secondly, the large amount of hydriodic acid transforms the methylisobutylcarbinol almost entirely to methylisobutyl iodide, and thereby gives the maximum amount of reducible material, since the carbinol cannot be reduced. Thirdly, the hydriodic acid aids in the evolution of hydrogen from the zinc. Fourthly, the excess of hydriodic acid adds to any hexylene which may be formed and, by transforming it into hexyl iodide, again brings it back into the sphere of action.

Methylisobutylpinacone.

The high-boiling fraction obtained as a by-product from the reduction of methyl isobutyl ketone, was twice distilled, the boiling point was 240° – 255° the first time, but on redistillation it became constant at 245° . At ordinary temperatures it remained liquid.

The results of analysis and the method of formation show this compound to be a pinacone, with the formula,



Analysis :

0.1716 gram substance gave 0.4516 gram CO_2 and 0.1991 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{26}\text{O}_2$.	Found.
C	71.28	71.62
H	12.87	12.87

Properties.—A viscous, oily liquid with a moderately strong odor like salt mackerel. It is soluble in alcohol, ethyl acetate, acetone, ethyl ether, benzene and glacial acetic acid ; insoluble in water.

Reduction of Methylisobutylpinacone.

In a mixture of 10 grams of amyl alcohol (b. p. 116° – 118°) and 40 grams of glacial acetic acid, 7 grams of methylisobutylpinacone were dissolved. Into this solution, cooled to 0° , was

passed gaseous hydriodic acid from 44 grams of iodine,¹ and to it about 15 grams of zinc were added. The mixture was allowed to stand 5 days.

After this it was poured off from the remaining zinc into a flask with a side neck. On distilling over the free flame a few drops passed over at 70°–90° (hexane), while about one-half the total volume distilled at 100°–120°. On further heating, the temperature slowly rose to 170°, at which point the distillation was stopped. The residue was deep red in color. To the distillate was added 4 volumes of water, whereby a reddish colored oil separated out and sank to the bottom. This lower layer was drawn off, washed with water, dried with calcium chloride and distilled.

The first fraction distilled at 120°–135°, and consisted mainly of amyl acetate; the second boiled at 150°–170° and had an odor like an alkyl iodide, contaminated, however, by amyl acetate. To purify this second fraction, it was first washed with 60 per cent ethyl alcohol, then with pure water and finally dried with calcium chloride. On redistilling, it boiled almost constantly, but with some decomposition, at 158°–160° (760 mm.); 8 grams were obtained.

This compound is, undoubtedly, methylisobutylcarbinol iodide. The boiling point, 158°–160°, is what one would expect for such a substance, and it is easy to account for its formation from methylisobutylpinacene. The constitution, therefore, is $(\text{CH}_3)_2\text{CHCH}_2\text{CHICH}_3$. Analysis:

I. 0.2885 gram substance gave 0.3237 gram AgI.

II. 0.1138 gram substance gave 0.1265 gram AgI.

	Calculated for $\text{C}_6\text{H}_{13}\text{I}$.	I.	Found.	II.
I	59.87	60.63		60.07

Methylisobutylcarbinol iodide is a colorless, oily liquid, with the odor characteristic of alkyl iodides, it boils at 158°–160° with some decomposition and is insoluble in water, but dissolves in alcohol, ether and the common organic solvents.

¹ Gatterman: *Loc. cit.*

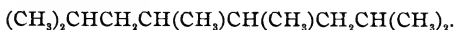
Dimethyldiisobutylethane.

The residue in the flask, after distilling off the methylisobutylcarbinol iodide, was treated with 6 volumes of water. A thin oily layer, which floated on the water, was separated. It was dissolved in ligroin (b. p. 40° – 70°) and the solution dried with calcium chloride. By distilling off the ligroin, a residue was obtained consisting of less than 1 cc. of colorless, oily liquid, which distilled at a little over 200° . By careful redistillation, the boiling-point 208° – 210° was determined as accurately as possible with such a small quantity. Analysis:

0.1234 gram substance gave 0.3846 gram CO_2 and 0.1673 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{26}$.	Found.
C	84.70	85.00
H	15.30	15.06

This analysis and the formation of the substance from methylisobutylpinacone show it to be the hydrocarbon, dimethyldiisobutylethane,



It is an oily liquid with a faint odor, soluble in ligroin but not very soluble in alcohol.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF CHLORIDE OF IODINE ON PYROCATECHIN.

BY C. LORING JACKSON AND M. C. BOSWELL.

The work described in this paper was undertaken in the hope of preparing tetraiodorthobenzoquinone, but none of the methods tried by us for making the tetraiodopyrocatechin have led to this substance. Of these, the action of monochloride of iodine on pyrocatechin seemed the most promising, because Michael and Norton¹ have found that this reagent converted resorcin into triiodoresorcin, but our experiments with these two bodies showed that the reaction was by no means so sim-

¹ Ber. d. chem. Ges., 9, 1752 (1876).

ple as in the case of resorcin, since much iodine was set free, and red products obtained, which were evidently formed by the union of several molecules of pyrocatechin. We could find no way for purifying these substances directly, but by reducing them with sulphurous dioxide, after the removal of the iodine, we succeeded in obtaining two white compounds, one melting at 224° , when a small proportion of the ICl had been used (10 : 90 ICl), the other melting at 252° , formed by a larger amount (10 : 120 ICl). Preliminary experiments indicated that still another compound, at least, could be obtained by varying the proportion of chloride of iodine, but that variations in the other conditions seemed to have no effect on the product.

Our analytical results with the substance melting at 224° leave us in doubt as to which of two formulas belongs to it, $C_{30}H_{19}O_{10}Cl_8I_3$ or $C_{26}H_{18}O_9Cl_7I_2$; the balance of evidence is in favor of the first, but it is impossible to decide between them by analysis alone, and our only analysis of a derivative, that of the acetyl compound, although declaring in favor of the first formula, is not absolutely decisive. We were unable to settle this point because our work was broken off before it was finished by the departure of one of us from Cambridge. Either of the compounds represented by these formulas might have been formed by the reaction, since the first consists of 5 molecules of pyrocatechin, in which part of the hydrogen has been replaced by the halogens, the second of 4 molecules of pyrocatechin, in which part of the hydrogen has been replaced by the halogens and an acetyl group. The hydrogen given in these formulas is the maximum amount, but it is probable that some of it has been eliminated in the process of uniting the molecules of pyrocatechin.

The supposition that a molecule containing 5 benzene rings would crystallize well and melt as low as 224° seems, at first sight, very improbable, but it is not without analogy in this class of compounds, as a derivative of tetrachlororthoquinone has been prepared by Mr. MacLaurin in this laboratory, which, as shown by molecular weight determinations, contains 4 benzene rings and melts at 210° .

As to the constitution of our octochlortriiodpentapyrocate-

chin, much more work will be necessary before it can be definitely settled, but we have established the following points with tolerable certainty: Oxidation with nitric acid converts it into a red substance, melting at 272° , crystallizing with toluene of crystallization, and acted on by most solvents. There can be little doubt, therefore, that it is an orthoquinone, probably the same as the dark red first product of the action of ICl on pyrocatechin. In that case the compound melting at 224° must contain two hydroxyl groups in the ortho position. Further, if in preparing this substance the reduction with sulphurous dioxide is carried on without removing the free iodine, the product is trichloropyrocatechin, undoubtedly due to the decomposition of the octochlor body by the hydriodic acid, which indicates that our substance contains one group $C_6HCl_3O_2$ at least. As has been already pointed out, it is probably analogous to the polymeric derivative of substituted orthoquinone discovered by Mr. MacLaurin, which it resembles closely in many properties.

The substance melting at 252° , obtained with a larger amount of ICl, gave analytical results agreeing with the formula $C_{18}H_{10}O_6Cl_7I$, and analysis of the acet derivative gave results also in agreement with this formula, but other derivatives should be analyzed before its composition is considered finally settled. Such a compound would be made up of three pyrocatechin molecules with part of the hydrogen replaced by the halogens, and therefore should be called heptachloriodtripyrocatechin. It is certainly strange that this tripyrocatechin compound melts at a higher temperature than the pentapyrocatechin compound, but this may be accounted for by the greater replacement of hydrogen by halogens in the former than in the latter.

If the tripyrocatechin is oxidized with nitric acid, it gives a red compound, probably an orthoquinone; and if, in preparing it, the reduction with sulphurous dioxide is carried on before the iodine has been removed, tetrachloropyrocatechin is formed, which crystallizes from water with $1H_2O$. The formula of the tripyrocatechin may, therefore, be developed as follows:



Consequently, our experiments show that the action of monochloride of iodine on pyrocatechin leads to the union of several molecules of it, for in no case did we obtain derivatives from a single molecule, except where, by reduction with sulphurous dioxide and hydriodic acid, the trichlor or tetrachlorpyrocatechin was obtained, and in view of all the facts observed these must have been formed by the breaking up of the more complex real products of the reaction. We ascribe this greater complexity of the reaction to the formation of orthoquinones, which have a great tendency to form such complex aggregates. That such quinones were formed was shown by the red color of the products and confirmed by the fact that much iodine was set free. The introduction of chlorine as well as iodine into the molecule is another marked difference between the action of chloride of iodine on pyrocatechin and on resorcin or aniline.

Many other methods for making tetraiodpyrocatechin or orthoquinone were tried, but none of them led to the desired result.

EXPERIMENTAL.

Action of Monochloride of Iodine on Pyrocatechin.

The chloride of iodine, ICl , used by us was made by passing washed and dried chlorine into a flask containing a weighed quantity of iodine, until the calculated amount of chlorine had been taken up, as shown by the increase of weight. This point was also indicated by the appearance of yellow crystals of the tetrachloride of iodine.

Compound Melting at 224° .—Thirty grams of pyrocatechin were dissolved in 900 cc. of glacial acetic acid and treated with 270 grams of monochloride of iodine, introduced by passing a stream of air through the flask containing it, which was heated on the water-bath to 50° – 60° . A precipitate of iodine was formed during the addition of the chloride and, after the required amount had been introduced, the dark colored liquid was poured off from this iodine and heated for an hour on the steam-bath, with vigorous shaking at intervals of 10 minutes,

when large quantities of hydrochloric acid were given off. Three or four liters of water were then added to the product, which precipitated a dark colored mass containing a great deal of iodine. This was next removed by rubbing it with a strong solution of potassic iodide and washing with water. The dark red residue could not be purified by any solvents which we could find, since they either converted it into light colored products, as in the case of dilute acetic acid or alcohol, or, if there was no chemical action, the solutions yielded no crystals. Accordingly, we proceeded as follows: The substance was dissolved in glacial acetic acid with the aid of a gentle heat, and a stream of sulphurous dioxide was passed through the solution, until a sample gave a white precipitate with water. The whole was then diluted and the solid thus obtained crystallized three times from alcohol, when it showed the constant melting point 224° , and was dried at 100° for analysis.

I. 0.3049 gram substance gave 0.3551 gram CO_2 and 0.0309 gram H_2O .

II. 0.3093 gram substance gave 0.3512 gram CO_2 and 0.0615 gram H_2O .

III. 0.2078 gram substance gave 0.2379 gram CO_2 and 0.0535 gram H_2O .

IV. 0.1892 gram substance gave 0.2883 gram $\text{AgCl} + \text{AgI}$, which yielded 0.2193 gram Ag_2S .

V. 0.1759 gram substance gave 0.2693 gram $\text{AgCl} + \text{AgI}$.

VI. 0.3191 gram substance gave 0.4875 gram $\text{AgCl} + \text{AgI}$.

	I.	II.	III.	IV.	V.	VI.
C	31.76	30.96	31.22
H	1.18	2.21	2.86
Cl_8^1	23.35	23.46	23.41
I_3	31.32	31.47	31.41

The analyses were made with specimens from more than one preparation.

¹ These results were calculated on the supposition that there are Cl_8I_3 in the compound. The proportion Cl_7I_2 is also possible; in that case the results become:

	IV.	V.	VI.
Cl_7	25.68	25.81	25.75
I_2	26.25	26.38	26.32

The determination of the relative amounts of chlorine and iodine was based on the conversion of the precipitate of $\text{AgCl} + \text{AgI}$ into argentic sulphide by the following method: The precipitate, after it had been weighed on a Gooch crucible, was shaken with the asbestos mat into a beaker and treated with a cold, strong solution of sodic thiosulphate, the crucible being washed with a portion of a similar solution. After all the silver salts had been dissolved in this way, ammoniac sulphide was added, the mixture allowed to stand over night and the Ag_2S dried at 110° on a Gooch crucible.

This indirect determination is so unfavorable that several different proportions of chlorine and iodine give results agreeing with the amount of argentic sulphide obtained, but when the other analytical numbers are brought into the calculation, only two proportions are found to be possible— Cl_8I_3 and Cl_7I_2 .

Weights of Ag_2S Corresponding to 0.2883 Gram $\text{AgCl} + \text{AgI}$ (Analysis IV.).

Calculated for		Found.
$8\text{AgCl} + 3\text{AgI}$.	$7\text{AgCl} + 2\text{AgI}$.	
0.2122	0.2183	0.2193

The second proportion agrees excellently with the experimental result, but the first, although not so good, is not far enough out to be rejected.

The two formulas derived from these proportions of the halogens give percentages which are compared with those from Analyses III. and VI. in the following table:

	Calculated for		Found.
	$\text{C}_{30}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$.	$\text{C}_{26}\text{H}_{18}\text{O}_9\text{Cl}_7\text{I}_2$.	
C	29.90	31.37	31.22
H	1.58	1.81	2.86
Cl_8	23.59	. .	23.41
I_3	31.64	. .	31.41
Cl_7	. .	25.00	25.75
I_2	. .	25.54	26.32

These results point to the formula $\text{C}_{30}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$ as the correct one, although the C is over 1 per cent too high for it, but in the presence of so much halogen this result is more probable than that according to Formula II., as this, in spite of the greater apparent agreement, requires more carbon than was

found. The percentages from Analysis I., to be sure, agree with the second formula, but the low hydrogen and high carbon in this analysis are so improbable that we feel inclined to reject it.

An acetyl derivative was made by heating the compound melting at 224° with a large excess of acetyl chloride on the steam-bath, for half an hour. The product was then precipitated with water, purified by recrystallization from dilute alcohol, and dried at 100° .

0.2115 gram substance gave 0.3160 gram $\text{AgCl} + \text{AgI}$.

Calculated for $\text{C}_{30}\text{H}_{17}\text{O}_{10}(\text{C}_2\text{H}_3\text{O})_2\text{Cl}_8\text{I}_3$.		Found.
Cl_8	22.05	22.90
I_3	29.57	30.72
Calculated for $\text{C}_{26}\text{H}_{16}\text{O}_9(\text{C}_2\text{H}_3\text{O})_2\text{Cl}_7\text{I}_2$. $\text{C}_{26}\text{H}_{17}\text{O}_9\text{C}_2\text{H}_3\text{OCl}_7\text{I}_2$.		Found.
Cl_7	23.04	23.98
I_2	23.55	24.51
		25.19
		25.74

These results, although they leave much to be desired, agree best with $\text{C}_{30}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$ as they stand, but the following considerations make them tell even more strongly in its favor. The white compound, melting at 224° , when oxidized with nitric acid, was converted into a red body melting at 272° , which showed the properties of an orthoquinone. The original substance was, therefore, probably the corresponding pyrocatechin, which, on treatment with acetyl chloride, would give a diacet body. If this supposition is true, the analysis is decisive in favor of Formula I., but, even if it is not, the evidence at hand is so strong for this formula, $\text{C}_{30}\text{H}_{19}\text{O}_{10}\text{Cl}_8\text{I}_3$, that it can be adopted, until further work has furnished decisive results. Such a compound would be made up of 5 molecules of pyrocatechin with part of the hydrogen replaced by chlorine and iodine. A substance having Formula II. would be made up of 4 molecules of pyrocatechin, in which part of the hydrogen was replaced by chlorine, iodine and one acetyl group; both, therefore, are compounds which might have been formed under the conditions of the reaction. The maximum amount of hydrogen is assumed to be present in these formulas; obviously a less amount might be nearer the truth.

If the formula $C_{30}H_{19}O_{10}Cl_8I_3$ is adopted for the substance melting at 224° , it would be called octochlortriiodpentapyrocatechin. It crystallizes from somewhat dilute alcohol in long, silky, white needles, which melt at 224° and are soluble in ether, benzene, or acetic acid. With nitric acid it is converted into a dark red substance (probably identical with the direct product from the action of chloride of iodine on pyrocatechin), which is very slightly soluble in the common solvents; but we succeeded in obtaining it from toluene in long, bright red needles, which grew darker on drying, probably from loss of toluene of crystallization, and then melted¹ at 272° . It showed a tendency to turn light yellow when treated with benzene, ligroin, or dilute acetic acid. These properties indicate that it is an orthoquinone.

Trichlorpyrocatechin.

In the process given for preparing octochlortriiodpentapyrocatechin, if the iodine was not removed from the crude product before the reduction with sulphurous dioxide, a different result was obtained, as shown by the following experiment, which was repeated several times: Thirty grams of pyrocatechin were dissolved in 500 cc. of glacial acetic acid and treated with 280 grams of chloride of iodine, either passed into the solution in a current of air or added in solution in acetic acid. The mixture, after standing over night, was heated on the steam-bath for half an hour and then treated with sulphurous dioxide and a little water (not enough to form a precipitate) until it was decolorized, when 1.5 liters of water were added and the voluminous, white precipitate, formed on stirring and cooling with ice, filtered out and purified by crystallization from hot water. Instead of melting at 224° this product melted at 115° and, after drying at 70° , at 134° – 135° . This indicated that it might be the trichlorpyrocatechin, which, according to Cousin,² melts, when dried, at 134° – 135° , but at 104° – 105° with its water of crystallization. We are unable to explain this difference of 10° between our melting point

¹ This melting point is subject to revision by later experiments on a larger scale.

² Bull. Soc. Chim., [3], 13, 719. Ann. Chim. Phys., [7], 13, 483.

and that of Cousin. The following analyses prove that it is this substance :

I. 1.1008 grams air-dried substance lost 0.0891 gram, when dried at 100° , but this loss was accompanied by decomposition, shown by the darkening of the specimen. This decomposition by heat was also observed by Cousin.

II. 0.3232 gram air dried substance gave 0.3641 gram CO_2 and 0.0549 gram H_2O .

III. 0.3102 gram substance gave 0.3557 gram CO_2 and 0.0723 gram H_2O .

IV. 0.2079 gram substance gave 0.3836 gram AgCl , which yielded 0.3325 gram Ag_2S instead of 0.3315 gram.

V. 0.2334 gram substance gave 0.4319 gram AgCl , which yielded 0.3710 gram Ag_2S instead of 0.3733 gram.

There can be no doubt, therefore, that the substance contained chlorine and no iodine.

	Calculated for $\text{C}_6\text{HCl}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$.	I.	II.	Found. III.	IV.	V.
H_2O	7.78	8.10
C	31.11	. .	30.70	31.27
H	2.16	. .	1.89	2.59
Cl	46.02	45.61	45.75

As this trichloropyrocatechin was obtained by the method, which gave the octochlorotriiodopentapyrocatechin, when the iodine was removed before reduction, it must owe its formation to the action of hydriodic acid and there can be little doubt that this consists in breaking up the complex molecule of the substance melting at 224° . If the reduction with sulphurous acid and hydriodic acid was long continued, water precipitated nothing from the acetic acid solution.

Compound Melting at 252° .—When, in treating pyrocatechin with chloride of iodine, the proportion of this reagent was raised from 135 grams to 180 grams for 15 grams of pyrocatechin; the other conditions remaining the same, a different compound was obtained which, after crystallization from hot, dilute alcohol, showed the constant melting point 252° , and, when dried at 100° , gave the following results on analysis :

I. 0.2720 gram substance gave 0.3085 gram CO_2 and 0.0363 gram H_2O .

II. 0.3133 gram substance gave 0.3595 gram CO_2 and 0.0763 gram H_2O .

III. 0.2259 gram substance gave 0.4046 gram $\text{AgCl} + \text{AgI}$, which yielded 0.3273 gram Ag_2S .

IV. 0.2318 gram substance gave 0.4150 gram $\text{AgCl} + \text{AgI}$, which yielded 0.3385 gram Ag_2S .

	Calculated for $\text{C}_{18}\text{H}_{10}\text{O}_6\text{Cl}_7\text{I}$.	I.	II.	Found.	III.	IV.
C	30.97	30.93	31.30	.	.	.
H	1.43	1.48	2.71	.	.	.
Cl	35.63	.	.	35.91	35.90	
I	18.21	.	.	18.35	18.34	

The 0.4046 gram of $\text{AgCl} + \text{AgI}$ (Analysis III.) gave 0.3273 gram Ag_2S . $7\text{AgCl} + \text{AgI}$ give 0.3238 gram Ag_2S .

0.4150 gram $\text{AgCl} + \text{AgI}$ (Analysis IV.) gave 0.3385 gram Ag_2S . $7\text{AgCl} + \text{AgI}$ give 0.3321 gram Ag_2S .

The acetyl derivative was also made by boiling with an excess of acetyl chloride for half an hour, precipitating with water and purifying by crystallization from hot, dilute alcohol. After drying at 100° it gave the following result:

0.1541 gram substance gave 0.2505 gram $\text{AgCl} + \text{AgI}$.

	Calculated for $\text{C}_{18}\text{H}_8\text{O}_6(\text{C}_2\text{H}_3\text{O})_2\text{Cl}_7\text{I}$.	Found.
Cl	31.80	32.60
I	16.25	17.65

A substance with the formula $\text{C}_{18}\text{H}_{10}\text{O}_6\text{Cl}_7\text{I}$ would be formed by the union of 3 molecules of pyrocatechin, in which part of the hydrogen had been replaced by the chlorine and iodine. The amount of hydrogen given is the maximum, but there may be a smaller quantity present. This heptachloriodtripyrocatechin crystallizes from hot, somewhat dilute alcohol in long, fine, white, silky needles, which melt at 252° and are less soluble in alcohol or acetic acid than the octochlor compound.

Tetrachlorpyrocatechin.

Fifteen grams of pyrocatechin were dissolved in 800 cc. of glacial acetic acid and treated with 180 grams of chloride of

iodine, introduced by means of a current of air, the liquid was then poured off from a quantity of iodine, that had been deposited, heated on the steam-bath, decolorized with sulphurous dioxide and water, and finally diluted with a large volume of water. At first there was no precipitate, but on standing over night long, white needles were formed, which melted at 193° – 194° ; tetrachlorpyrocatechin melts at 194° – 195° . This preparation should have given heptachloriodtripyrocatechin, if the iodine had been removed before reducing with sulphurous dioxide. That the substance is tetrachlorpyrocatechin was proved by the following analysis:

0.2156 gram air-dried substance gave 0.4670 gram AgCl, which yielded 0.4007 gram Ag_2S instead of 0.4035 gram. The silver salt is, therefore, AgCl.

	Calculated for $\text{C}_6\text{Cl}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$.	Found.
Cl	53.38	53.56

Tetrachlorpyrocatechin as prepared by Zincke¹ and by Zincke and Küster² was anhydrous, since it was crystallized from glacial acetic acid. We, accordingly, determined the amount of water of crystallization in our preparation:

0.6825 gram air-dried substance lost 0.0424 gram when dried at 110° .

	Calculated for $\text{C}_6\text{Cl}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$.	Found.
H_2O	6.77	6.21

If in this reduction with sulphurous dioxide, in presence of iodine, the reducing action is long continued, water precipitates nothing from the product.

The conditions under which the chloride of iodine acted on the pyrocatechin were varied in many ways, but the only variations which seemed to affect the product were in the proportion of the two reagents and the nature of the solvent. The concentration of the solution had no effect, unless it was so great that the reaction became too violent, producing de-

¹ Ber. d. chem. Ges., **20**, 1779 (1887).

² *Ibid.*, **21**, 2729 (1888).

composition. Temperatures from 0° to 100° did not modify the product, but it was found that the reaction ran very slowly below 60° . The chloride of iodine could be introduced indifferently in a stream of air, in solution in acetic acid, or directly from a drop funnel. When water or chloroform replaced the acetic acid as the solvent, the product was tarry and gave, with benzene and ligroin, reddish brown crystals, which seemed to be different from those obtained with acetic acid.

As already shown, different proportions of chloride of iodine gave different products, and we have reason to suppose that several other substances might be obtained by varying these proportions still further. This was indicated by the following preliminary experiments: Five grams of pyrocatechin, dissolved in 85 cc. of acetic acid, were treated with 75 grams of chloride of iodine (a much larger excess than any used above) and allowed to stand 3 days, precipitated with water and, after 3 hours, the deposit filtered out and recrystallized from alcohol, when it showed the melting point 270° . Perhaps the same substance was obtained from the alcoholic mother liquors in purifying the product melting at 252° . The aqueous filtrate, in the preparation described above, also seemed to contain another substance.

A solution of 2.5 grams of pyrocatechin in 15 cc. of acetic acid was added, very slowly, to a solution of chloride of iodine in about 3 times the amount of acetic acid, and heated on the steam-bath. Much iodine was precipitated and the hot liquid poured off from this deposited beautiful needles, which turned white after washing with potassic iodide. This product differed from all the others in being unaffected by nitric acid, while the others are reddened by oxidation. We tried many times to prepare this substance again, but without success.

After we were convinced that tetraiodpyrocatechin could not be made with chloride of iodine acting on pyrocatechin, the following unsuccessful experiments were tried with other processes: Iodine was allowed to act on pyrocatechin either alone or with iodic acid, plumbic oxide, or mercuric oxide, in solution in water, alcohol, ether, or acetone, cold or hot, but

without any formation of tetraiodpyrocatechin. With iodic acid the pyrocatechin was charred; with the metallic oxides there was no action. Fuming sulphuric acid and iodine decomposed the pyrocatechin. Tetrachlorpyrocatechin, in alcoholic solution, was boiled for 2 days with potassic iodide, without action. Pyrocatechin diacetate gave, with chloride of iodine, the same results as pyrocatechin itself.

CAMBRIDGE, MASS.,
March 20, 1906.

THE COMBUSTION OF HALOGEN COMPOUNDS IN PRESENCE OF COPPER OXIDE.

BY CHARLES J. ROBINSON.

In the course of some work by J. Bishop Tingle and the author of this note, occasion arose for determining carbon and hydrogen in certain compounds containing a halogen, and an attempt was made to do away with the necessity for preparing a combustion tube filled with lead chromate by suitably modifying the ordinary tube containing copper oxide. This purpose was accomplished simply and satisfactorily in the following manner:

A cartridge, similar to that employed by Morse and Taylor¹ in the analysis of sulphur compounds, was made by rolling a small piece of heavy copper wire gauze into the form of a hollow cylinder, which was only 6 or 7 cm. long, and just fitted into the combustion tube. The cylinder was filled with pure lead chromate, the ends closed by wrapping with copper wire, which also passed lengthwise through the cartridge, and was looped at each end to facilitate removal from the tube. The copper parts were oxidized by ignition. When it was desired to analyze halogen compounds, this cartridge was placed just in front of the boat, in a combustion tube filled in the ordinary way with copper oxide. In burning, care was taken that the part of the tube containing the cartridge was well heated before decomposition of the substance began, but no other special precautions were found necessary. If the space in the tube, or the decomposition temperature of the substance

¹ THIS JOURNAL, 33, 602.

to be analyzed demand it, the oxidized spiral in front of the boat should, of course, be removed and the cartridge be allowed to occupy its place.

The advantages gained by the use of this device are that combustions of halogen compounds can be made just as readily as combustions of ordinary compounds, and that the same tube can be used for both. The cartridge may be removed or not, as the operator pleases, to make ordinary analyses subsequent to analyses of substances containing halogens. The same cartridge may be used repeatedly, but no statement can be made as to the number of times it can be employed safely without renewal, because of the great variation in content of halogen in different compounds. The life of the tube itself is not affected as it is when the tube is entirely filled with lead chromate.

The method has been found to be so completely satisfactory that it is judged decidedly preferable, in very many cases, to determine carbon and hydrogen rather than halogen for the identification of new compounds. The time required for the analysis is much shorter, and the figures for the content of carbon and hydrogen in complex bodies are usually much more distinctive than those for the content of halogen.

No special experiments have been conducted to test the method, but the analyses given below were made in the course of the investigation referred to. The substances analyzed are products of the action of *p*-bromophenylhydrazine on camphor-oxalic acid. Only the one determination of carbon and hydrogen was made in each case.

I. A compound $C_{18}H_{23}O_4N_2Br$, melting at 149° with decomposition.

0.2409 gram substance gave 0.4603 gram CO_2 and 0.1150 gram H_2O .

	Calculated.	Found.
C	52.53	52.14
H	5.63	5.34

II. A compound $C_{18}H_{21}O_3N_2Br$, melting at 172° with decomposition.

0.2135 gram substance gave 0.4308 gram CO_2 and 0.0982 gram H_2O .

	Calculated.	Found.
C	54.94	55.03
H	5.38	5.15

III. A compound $C_{20}H_{23}O_2N_2Br$, m. p. 107° .

0.2125 gram substance gave 0.4624 gram CO_2 and 0.1045 gram H_2O .

	Calculated.	Found.
C	59.52	59.35
H	5.75	5.50

IV. A compound, $C_{18}H_{19}O_2N_2Br$, melting at 215° with decomposition.

0.1937 gram substance gave 0.4095 gram CO_2 and 0.0923 gram H_2O .

	Calculated.	Found.
C	57.58	57.66
H	5.10	5.33

The method has also been applied to the determination of nitrogen in halogen compounds. The cartridge of lead chromate is placed just in front of the substance to be burned, and the latter is mixed with lead chromate. Otherwise the tube is filled in the ordinary way with copper oxide. The results obtained are shown in the following analysis:

I. The compound $C_{18}H_{21}O_3N_2Br$.

0.2624 gram substance gave 16.2 cc. N_2 at 19° and 758 mm.

	Calculated.	Found.
N	7.14	7.08

The determination of carbon and hydrogen in sulphur compounds could, doubtless, be accomplished in the same manner, in the presence of copper oxide, but no experiments have been made in this direction.

OBITUARY.

PIERRE CURIE.

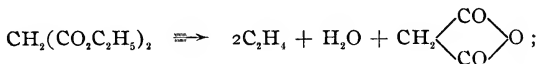
Professor Pierre Curie was born May 15, 1859, and was knocked down and killed by a wagon in Paris, April 19, 1906. Curie received his education in Paris and in 1895 obtained the degree of Doctor of Science from the University there. At the time of his death he was professor of general physics at the École Municipale de physique et de chimie industrielles, professor of physics in the Faculty of Sciences, University of Paris, and member of the Académie des Sciences of the Institute of France. He was also an honorary member of various foreign scientific societies. This is not the place to detail Curie's purely physical work; to chemists he is best known by his researches in the field of radio-activity. His earliest paper on this subject appeared in 1898; it was written in conjunction with Madame Curie and led her to the discovery of polonium and radium. Curie was the first to observe that radium constantly evolves heat and he measured its amount. He also showed that the radiations of radium consist of two kinds; he determined the emanating power of radium compounds and, following Ramsay, proved that helium is produced from radium.

REPORTS.

A New Oxide of Carbon, C₃O₂. Carbon Suboxide.

What is, in many respects, one of the most interesting discoveries which has been made for several years, has recently been announced from E. Fischer's laboratory by Otto Diels and Bertram Wolf.¹ By the action of phosphorus pentoxide on ethyl malonate vapor at about 300°, in an apparatus of special construction, they have succeeded in obtaining an anhydride of malonic acid.

In view of what is known of the action of phosphorus pentoxide on esters, one or the other of the following equations must represent its action on ethyl malonate:





That the new compound is formed according to the second equation is proved by its vapor density, composition and properties.

Carbon suboxide is a colorless, highly refractive, volatile liquid, which boils at 7° and has an odor resembling that of acrolein and oil of mustard. It rapidly attacks the eyes, throat and respiratory organs and, when breathed in quantity, produces symptoms of suffocation.

Chemically, carbon suboxide acts essentially as an anhydride of malonic acid, but it also exhibits certain affinities to the carbonyl compounds such as $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$,¹ and is to be regarded as carbon carbonyl. It burns with a very smoky, intensely blue flame and reacts rapidly with water to form malonic acid; with dry hydrogen chloride malonyl chloride is formed, while aniline and ammonia yield malonanilide and malonamide, respectively.

Carbon suboxide decomposes spontaneously at 15° , in the course of a day or two; the liquid becomes yellow, deposits a solid, darkens and finally is completely transformed into a dark red solid. This readily dissolves in water with an eosin-red color.

At 37° the transformation of the carbon suboxide is much more rapid, the product being very hard, and deep black-red in color. In part it dissolves in water, giving a dark brown solution. At 100° the decomposition of carbon suboxide is instantaneous. These decomposition products are probably similar to the compounds C_4O_3 and C_8O_3 , or, possibly, they are identical with them. The two substances in question were described by Brodie and by Berthelot about 30 years ago; the former was prepared by the action of a silent electric discharge on carbon monoxide and the latter by heating C_4O_3 .

J. BISHOP TINGLE.

Amino Acids, Polypeptides and Proteids.

In a lecture given recently before the German Chemical Society, Emil Fischer² summarizes the results obtained from the researches which he has carried out on the above substances during the past 6 years. His work began with a study of the amino acids; at that time only 9 monamino acids, 3 diamino acids, and cystine, which contains sulphur, had been recognized as decomposition products of proteids; 8 racemic modifications of these monamino acids had been synthesized.

The two most general practical methods which were known were

¹ THIS JOURNAL, 35, 469 (1906).

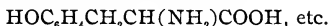
² Ber. d. chem. Ges., 39, 530 (1906).

the action of ammonia on α -halogen aliphatic acids and that of ammonia and hydrogen cyanide on an aldehyde. Fischer has improved the former method by brominating alkyl malonic acids, obtaining $\text{RCBr}(\text{COOH})_2$, which, when heated, yields a brom aliphatic acid. Among other important compounds, α -aminocaproic acid (leucine),

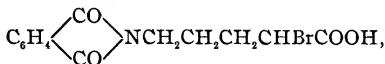


was prepared by this method.

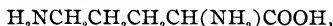
With the exception of glycocoll, all the amino acids obtained from proteids contain an asymmetric carbon atom and are optically active, but the synthetical products are, of course, racemic. Fischer's method of resolving these latter is beautifully simple; the benzoyl or formyl derivatives are prepared; these are strong acids, their salts with optically active bases can readily be separated by crystallization and the optically active form of the original acid may then be obtained by hydrolysis. The list of optically active acids prepared in this manner is already lengthy and includes α -aminopropionic acid (alanine), $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, α -aminocaproic acid (leucine), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, β , p -hydroxyphenyl- α -aminopropionic acid (tyrosine),



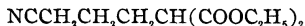
The synthesis of the diamino acids is a much more difficult problem than the preparation of monamino acids. Fischer has introduced marked improvements into two of the existing methods. The following example will serve to illustrate the first one: Ethyl phthaliminopropylmalonate readily yields a brom derivative which, when hydrolyzed and heated, gives phthaliminobromovaleric acid,



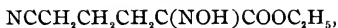
by the action of ammonia and the removal of the phthalyl group α , δ -diaminovaleric acid,



is formed. A better method for obtaining acids of this class depends on the action of nitrous acid on cyanalkyl malonates thus:



yields



which, when reduced by means of sodium and alcohol, yields α,ϵ -diaminocaproic acid (racemic lysine),



A third method consists in the addition of ammonia to acids containing 2 ethylene linkages.

The hydroxyamino acids having also been found in the decomposition products of proteids, it became necessary to improve the available means of obtaining them synthetically. Fischer found that Strecker's method, consisting in the combined action of ammonia and hydrogen cyanide, could be applied to the hydroxy aldehydes, the resulting cyanhydrin being then hydrolyzed. In this manner α -amino- β -hydroxypropionic acid (serine), $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$, was prepared from glycollic aldehyde. The same reactions have also been used to obtain certain derivatives of galactose and arabinose.

An extensive study had to be made of various derivatives of the amino acids in order to devise new processes for their isolation, recognition, purification, separation and condensation, and attention was naturally directed to the acyl derivatives. Although hippuric acid is readily obtained from aminoacetic acid, benzoyl chloride and sodium hydroxide, this method is not applicable to the majority of amino acids, but the use of sodium bicarbonate instead of the hydroxide frequently gives good results. Formyl derivatives can be obtained even more readily by boiling the amino acid with anhydrous formic acid. The use of these acyl derivatives for the resolution of racemic compounds has been mentioned above. Acetyl derivatives are not very satisfactory, but benzenesulphonic chloride and, particularly, β -naphthalenesulphonic chloride have proved to be of great value in the separation of mixtures of amino acids, unfortunately, however, the resulting sulphonyl derivatives are only hydrolyzed with difficulty. Phenylisocyanate and α -naphthylisocyanate frequently yield derivatives of the amino acids which crystallize readily.

The first important work on the esters of amino acids was done by Curtius, who demonstrated their ease of formation by the action of alcohol and hydrogen chloride, and studied a few of their reactions. Fischer found that many of these esters could be readily isolated from the ester hydrochlorides by the action of alkali, at low temperatures, and that the free esters thus obtained could be employed for the separation and purification of the amino acids, partly on account of differences in

boiling point under greatly reduced pressure, partly from their varied solubility. These esters, unlike the acids, have basic properties only and are highly reactive, derivatives have been obtained of some of them with acid chlorides, anhydrides, halogen alkyls, isocyanates, alkylthiocarbimides (mustard oils), aldehydes, ketones, carbon bisulphide, carbonyl chloride and ammonia. Certain of these compounds are of considerable interest, but of even greater importance was the preparation of the chlorides of such amino acids, because these chlorides could be used in the synthesis of polypeptides. After many unsuccessful efforts, it was found that the desired result could be obtained by the action of phosphorus pentachloride, in acetyl chloride solution, on the finely divided acid hydrochloride. This reaction has only been applied to acids with one amino and one carboxyl group; it has uniformly succeeded with them, but, oddly enough, it fails absolutely with amino-acetic acid which has been crystallized from water, no matter how completely the acid may be subsequently powdered and dried. The products have the formula $RCH(NH_3Cl)COCl$. Diamino and hydroxyamino acids give phosphorus derivatives under the above conditions.

Fischer gives, in some detail, the processes he has found to be of most service in the separation of individual acids from mixtures. The first step is to esterify, by the method already referred to, and then to fractionate under greatly reduced pressure, down to 0.5 mm. This not only effects a fairly good separation of individual esters, but serves to remove inorganic substances, complicated amino and hydroxyamino acids and polypeptides. The individual fractions are then further differentiated by means of their own varied solubility, by that of the free acids, by the use of phenylisocyanate, or by the preparation of naphthalenesulphonic acid derivatives, etc. The diamino acids, as is well known, are usually separated by means of phosphotungstic acid, but this method must be used with care or they will be contaminated by monoamino compounds. The first section of the lecture concludes with a summary of the methods of separation used for more than 30 of the more important compounds, together with full references to the literature.

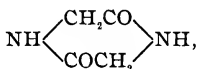
The second part of the lecture is devoted to the polypeptides, *i. e.*, amide derivatives of amino acids. The simplest representative of this class of substances is glycylglycine,



the prefixes di, tri, tetra, etc., indicate the number of acid

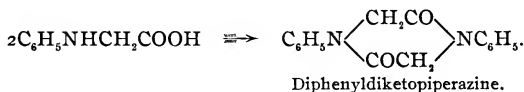
radicles present in any such compound. The term "peptide" is derived from peptone. Fischer regards his synthetic polypeptides as very closely related to natural peptones, indeed he believes that these latter consist, essentially, of mixtures of polypeptides.

The synthetical products allied to polypeptides, which had been obtained before Fischer began his work, were amorphous and poorly characterized. Curtius' open chain compounds were well defined and crystalline, but they all contained the benzoyl group; however, he succeeded in obtaining the simplest diketopiperazine,

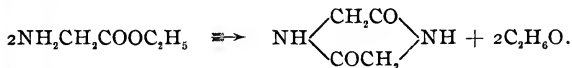


from ethyl aminoacetate, a matter of great importance for the chemistry of the dipeptides. The following synthetical methods have been employed in Fischer's work, some have been devised by him, others were already known :

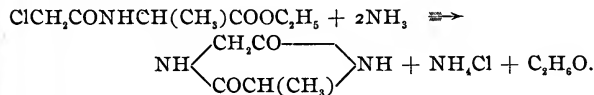
(I) *Synthesis of Polypeptides from Diketopiperazines.*
Synthesis of Diketopiperazines.—(i) Dehydration of amino acids by heating them in a current of carbon dioxide or hydrogen chloride :



(ii) Transformation of the esters of amino acids in aqueous solution :



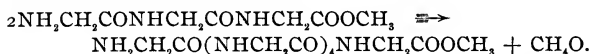
(iii) The action of ammonia on the esters of amino acids which contain an α -halogenated acyl. Thus, ethyl chloracetyl- α -aminopropionate (chloracetylalanine ester) gives methyl diketopiperazine,



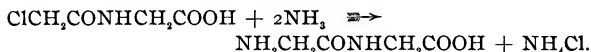
This method is widely applicable and of great practical importance.

These diketopiperazines are converted into dipeptides when hydrolyzed by means of hydrochloric acid or alkali, the latter being preferable and, indeed, essential in the case of the more complicated members of the series.

(II) *Synthesis of Polypeptides by Means of Esters.*—This promises to be of considerable use in the production of complicated compounds; the nature of the reaction is shown by the production of the methyl ester of hexapeptide from the methyl ester of diglycylglycine:

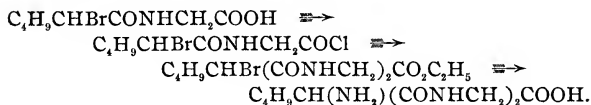


(III) *Synthesis of Polypeptides by Halogen Acyl Derivatives.*—A halogen acyl is introduced into an amino acid and the product, or its ester, treated with ammonia:



The glycylglycine thus obtained may be again treated with a halogen acyl chloride and the process repeated; this has already led to the production of pentapeptides and there is, as yet, no sign of any limit being reached. A little consideration will show the enormous number of compounds which are rendered accessible by this method.

(IV.) *Synthesis of Polypeptides by Linkage to the Carboxyl Group.*—In its results this may be regarded as an extension of the preceding method. Halogen acyl amino acids are treated with phosphorus pentachloride, in acetyl chloride solution; the resulting acid chloride readily reacts with the esters of amino acids or with polypeptides; the product is hydrolyzed and treated with ammonia and a new polypeptide obtained. Thus, α -bromisocaproylglycine (isobutyl δ -bromacetyl glycine) with ethyl aminoacetate gives, finally, leucylglycylglycine:



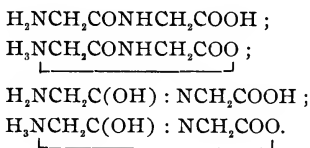
This method is also capable of wide application.

Natural proteids and their decomposition products, such as albumoses, peptones, etc., are all optically active, therefore the

synthesis of optically active polypeptides is a matter of considerable importance and interest. Of various methods which have been tried, the one which appears to be of the most general utility is by the use of the chlorides of active amino acids (*vide* p. 540).

Up to the present time about 70 polypeptides have been synthesized; the most complicated is the hepta derivative, leucylpentaglycylglycine.

The structure of polypeptides and of diketopiperazines is anything but a simple matter. To prove that they consist of amino acids with amide linkages by no means exhausts the subject, as shown by the fact that there exists no method for distinguishing between the following 4 formulæ for glycylglycine :



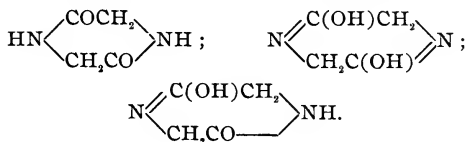
For the sake of simplicity, the first formula has been assumed in all the work that has been published up to the present. The possible complications of structure are, of course, greater in the case of the aminodicarboxylic and the diamino acids.

A peculiar kind of isomerism has been observed with some compounds, thus glycylglycinecarboxylic acid,



yields 2 *neutral* esters.

Finally, it may be pointed out that 2,5-diketopiperazine itself may have 3 possible structures, represented by the formulæ :



A most interesting discussion of the configuration of polypeptides and of the 2,5-diketopiperazines is given in the lecture, but space will not permit of its reproduction; it will suffice to say that the new compounds offer an unparalleled

wealth of material for testing the general theory of optically active carbon compounds; hitherto the results which have been obtained are in strict agreement with the current theory.

The second part of the lecture concludes with an account of the general properties and reactions of polypeptides; allusion to the more important of these has been made in the foregoing pages.

Fischer devotes the third part of his lecture to the proteids, and gives first a rather full description of his "ester method" for the separation of the products of acid hydrolysis. Briefly, this consists in hydrolyzing the proteid with hydrochloric acid and esterifying the highly concentrated product by means of alcohol and hydrogen chloride, the resulting esters being separated, first by distillation under greatly reduced pressure, then by special methods which have been referred to in the earlier pages of this report. Detailed directions are given for the isolation and identification of the more frequently occurring monamino acids.

The most important result of the employment of the ester method has been the comparatively easy isolation, from the hydrolysis products of proteids, of constituents which had previously been overlooked, or which could only be separated when they were present in relatively large quantity. A list is given of 21 proteids which have been investigated in this manner by Fischer and his students. He has also examined the products of the action of ferments, such as pepsin and pancreatin, on proteids and has investigated the substances obtained by the hydrolysis of casein by means of potassium hydroxide.

In considering the constitution of the proteids, the question has been raised as to whether the amino acids which result from their fermentative decomposition are preformed in the molecule; Fischer is firmly of the opinion that they are.

His work on the peptones and albumoses, so far as it has progressed, shows that the substances formed by their resolution are essentially similar to those from the proteids, other chemists who have investigated this subject and who have obtained somewhat different results, have always attempted to separate their products by precipitation, a method which is quite inadequate.

Regarding the structure of the proteids but little can be said; undoubtedly the connection of the amino acids with the proteid molecule is by an amide linkage, but to admit this is far from exhausting the possibilities; probably there are piperazine rings, which are known to open very easily, while the hydroxyl groups of the hydroxyamino acids undoubtedly play an important part in the structure and reactivity of the proteids.

Kossel's suggestion that *all* albuminoid compounds contain a "protamine nucleus" is hardly supported by the general results of Fischer's work.

It is abundantly evident that the territory which Fischer has entered will require, for its comparatively complete exploitation, the combined labor of numerous chemists extending over many years, and that it will involve the preparation of an enormous number of new compounds, the question arises, therefore—Will the results be likely to justify this expenditure of time, money and energy? Perhaps the most important effect of such researches will be that the experience and knowledge gained in the investigation of the synthetical compounds, may permit of the isolation and artificial preparation of the constituents of natural peptones and albumoses, in a manner similar to the production of glycine-*d*-alanine anhydride from silk, which is the first example of such a result. This phase of the work alone will involve an enormous amount of work, on account of the varied composition of the different proteids. The synthetical production of the true albumins is a problem of very much greater difficulty and, for its solution, entirely new methods of attack will have to be discovered. Even when this has been accomplished the further question will arise as to the value of the results to biology. Undoubtedly their worth will depend on the method of synthesis employed. Should the production of the new compound depend on a mere accident, such, for example, as the production of a proteid identical with one found in nature, by fusing an amino acid with a dehydrating agent, the result would be of but little value to the chemistry of the albumins and of practically none to biology. The slower method, however, attended with a thorough exploration of the properties of the individual compounds, should go far to clear up the behavior of proteids, ferments, toxins, etc.

J. BISHOP TINGLE.

REVIEWS.

CONVERSATIONS ON CHEMISTRY. First Steps in Chemistry. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Authorized translation by STUART K. TURNBULL. Part II.: The Chemistry of the Most Important Elements and Compounds. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall. 1906. Price, \$2.00.

The first volume of this book, treating of general chemistry, was recently reviewed in this JOURNAL.¹ In the present volume Ostwald talks of the elements and their compounds, of

¹ THIS JOURNAL, 34, 255.

acids and bases, of combining weights and gaseous volumes, as well as of atoms and molecules and of electrolytes. These and other matters are fully, admirably and luminously treated—from his point of view.

Teachers of chemistry who realize how difficult it is to present chemical fact and theory, in the lecture room or laboratory, in a really clear and simple way, will do well to read this book with close attention; it is profitable to study the author's methods of presentation, and especially profitable when his method differs essentially from that in common use. His explanation of the atomic theory and of gaseous volumes is particularly interesting and clever. To quote a few sentences, referring to the law of combining weights:

Master—"What then requires explanation in this law?"

Pupil—"Really nothing; but I thought there might perhaps be something especial in the background behind such a remarkable law."

M.—"Just so! Of course this is quite a childish idea like that of the peasant who, when they tried to explain the locomotive to him, said: 'I understand all that very well; but then, where really is the horse which drags all these wagons?'"

P.—"Ha, ha, ha! He was stupid!"

M.—"Not so very. He had no experience of the fact that we can set a wagon in motion otherwise than with a horse yoked on in front, and therefore he supposed that he would be able to understand the locomotive only after they had showed him the hidden horse. In point of fact, chemists have, for the last hundred years, assumed that there is such a hidden horse in the law of combining weights."

P.—"A horse! What does that mean?"

M.—"I speak figuratively. I mean that formerly it was necessary just in the same way for people to assume some such cause as regards the law of combining weights; because without it they could not put into expression the existence of such a law,—just as the peasant could not express to himself the idea that a train can get in motion without a horse."

P.—"Then what does the chemical horse look like?"

M.—"You know already; it is the atom."

What the master says is always well put, but the objectionable pupil is always "butting in," as he would say were he an American pupil. The author should rewrite the book and eliminate him, for he has no semblance of a live boy, but is an automaton, wound up to put the desired question at the proper moment, to be preternaturally acute when this acuteness acts as a foil to the thickheadedness of "other chemists," to be pre-

ternaturally dull when especial emphasis and repetition is desired, and to throw in a slang expression, or would-be naive remark every few pages.

While the function of the pupil was doubtless suggested by Socratic dialogue, his actual performance is largely that of Jules Verne's comic Frenchman. Readers of Jules Verne will recognize that his different books are made—in the literary sense—by one receipt; among the ingredients are the scientific man, who doles out the science which justifies the trip to the moon or elsewhere, or whiles away the time en route, and the comic Frenchman, whose function is to enliven the science of the scientific man by jokes and gambols; and this is often the function of the pupil; in Ostwald's words, he is to render the book "penetrating and lively."

In the review of the first volume the reviewer attempted to thus benefit his review by quoting the pupil's quips. On the same principle he ventures to enliven the close of the present review by the merry jest which lies in the last words of the master:

P.—"Tell me could I not get some book to read as a preparation for my future studies?"

M.—"I see; your talk about preparation is merely an excuse to find out what lies beyond. However I have no objections to make; self-chosen work usually gives not only more pleasure, but better results than a set task. At the present day we are rather awkwardly situated as regards chemical textbooks. During the last 15 years a great change has sprung up in our views and acceptance of science, and most of our literature is written in accordance with earlier ideas. I have directed your studies along the lines of modern thought, and to unlearn them by changing to the old style would cause you a great deal of unnecessary difficulty. So there is really only one book I can recommend to you as being quite up to date; it is 'Outlines of General Chemistry,' by W. Ostwald. The subject matter is more difficult than what you have been accustomed to; but it will answer many of the questions whose explanations I have, so far, had to reserve."

P.—"That is just the book I want."

Oh, Disciples of the Master! Bearers of light into dark places! Preachers and Publishers of the Word to "other chemists!" Is *this* your reward?

E. R.

CHEMIE DER ALICYKLISCHEN VERBINDUNGEN. Von OSSIAN ASCHAN, A. O. Professor an der Universität Helsingfors. Braunschweig: Fr. Vieweg und Sohn. 1905. pp. xlv + 1164. Price, M. 40.

This admirable work, which is dedicated to Professor von

Baeyer, in celebration of his seventieth birthday, was planned as the result of the author's labors on the last German edition of the organic portions of Roscoe and Schorlemmer's "Treasure." The scope and nature of the book can best be shown by an abstract of the table of contents. The general part (I.) comprises 386 pages, divided as follows: Introductory, pp. 7; Theoretical development of the chemistry of alicyclic compounds, pp. 228, divided into 12 chapters; Influence of ring formation on the chemical nature of alicyclic compounds, pp. 26, 2 chapters; Influence of ring formation on the physical properties of alicyclic compounds, pp. 65; The stereochemistry of alicyclic compounds, pp. 60, 4 chapters. The special part (II.) of 778 pages, is devoted to the Methods of formation and preparation of the alicyclic compounds, arranged systematically, pp. 39, 10 chapters; Monocyclic compounds, pp. 459, 6 chapters; Bicyclic compounds, pp. 213, 6 chapters; Tri- and Polycyclic compounds, pp. 36. The index, pp. 30, is admirably full. Only an extensive use of the book can show how far it has been possible to exclude errors; at the most they can but be of a trifling nature.

The plan of writing monographs on special branches of chemistry is an entirely good one, especially if the author is an acknowledged authority on the subject, as in the present case, but, for complete success, it is necessary that the collection of material should be as exhaustive as possible and that it should be clearly and systematically arranged, the style should be attractive and, wherever it can be done, the gaps in our present knowledge of the subject should be indicated and fresh lines of research suggested. Judged by all these criteria, the volume under review is an unqualified success; the author's name is a thorough guarantee of his competency for the work, and the brief synopsis given above shows how completely the subject has been covered and how admirably the material has been arranged. As an indication of the amount of labor involved, it may be mentioned that the book includes more than 5,000 citations, which are brought down to August, 1905. The style of the book is most pleasing—there is nothing of the "dry-as-dust" order about it. The first 12 chapters, dealing with the general theory of alicyclic compounds, treat the subject historically and are extremely fascinating reading. The author points out the urgent need for more work on the physical properties of these compounds, in many cases no data whatever are available, and frequently the statements in the literature are incorrect and contradictory. In other parts of the book, too, lines of fruitful inquiry are indicated. This volume may serve as a model

of what such a work should be; the author has placed his fellow-chemists under a debt of gratitude by producing it, and he is to be warmly congratulated on its successful completion.

J. B. T.

DIE ELEKTROLYSE GESCHMOLZENER SALZE. Zweiter Teil: Das Gesetz von Faraday; Die Überführung und Wanderung der Ionen; Das Leitvermögen. Von RICHARD LORENZ., Dr. phil., o. Professor für elektrochemie und physikalische Chemie am eidg. Polytechnikum in Zurich. Mit 59 in den Text gedruckten abbildungen. Halle a. S.: Druck und verlag von Wilhelm Knapp. 1905. pp. 257. Price, M. 8.

This book, which is Volume 21 of the "Monographs on Applied Electrochemistry," deals with a subject which is somewhat removed from the ordinary—the electrolysis of fused salts. It has long been known that, at elevated temperatures, dissociation into ions takes place, and that fused salts conduct the current. The literature on this subject has, until the present, been rather widely scattered. In this monograph Lorenz has brought together, in a very satisfactory form, what is known on the whole subject.

The larger divisions, under which the subject-matter is classified, are: The Law of Faraday; The Transference and Migration of the Ions; Conductivity.

From this it will be seen that the same general plan is followed as in dealing with the electrolysis of solutions.

The volume in question is a valuable addition to the already valuable series of monographs.

H. C. J.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS, Based upon the Application of the Theory of Electrolytic Dissociation and the Law of Mass Action. By E. H. S. BAILEY, PH.D., Professor of Chemistry, and HAMILTON P. CADY, PH.D., Assistant Professor of Chemistry in the University of Kansas. Fifth edition, thoroughly revised. Philadelphia: P. Blakiston's Son & Co. 1905. Price, \$1.25 net.

The fourth edition of this book appeared in 1901 and was reviewed in this JOURNAL¹ by Professor H. C. Jones. It will suffice to say here that it is a good laboratory manual, written in accordance with the theory of electrolytic dissociation, treating of the detection and separation of cations and anions, instead of metals and acids, and has, as a positive advantage, the benefit of the explanation offered by physical-chemical theory of certain analytical reactions.

E. R.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE. Von PROF. DR. A. BERNTHSEN. Neunte auflage bearbeitet in Gemeinschaft mit DR. ERNST MOHR. Braunschweig: Fr. Vieweg und Sohn. 1905. pp. xxii + 638. Price, M. 11.

This excellent text-book is so well known that a review of

¹ THIS JOURNAL, 27, 157.

the new edition may be confined to a statement of the changes and improvements which it contains. The text has been thoroughly revised, new matter having been added and certain portions of the old eliminated; this, in itself, has not involved an increase in the size of the book, the extra number of pages in the present edition being due to the use of large type for certain paragraphs which were formerly set more closely. The most important alteration, however, is in the division of the compound, into three classes, *viz.*, methane derivatives pp. 283, isocyclic derivatives pp. 198, and heterocyclic derivatives pp. 80; this arrangement is logical and should be of considerable benefit to the users of the book; the general introductory portion occupies 40 pages. The author is to be congratulated on these alterations. The production of the ninth edition shows that the work has obtained the recognition and appreciation which it so justly merits.

J. B. T.

THE PRODUCTION OF ALUMINUM AND ITS INDUSTRIAL USE. By ADOLPHE MINET, Officer of Public Instruction and Editor of "L'Electrochimie." Translated, with additions, by LEONARD WALDO, S.D. (Harv.). First edition, first thousand. New York: John Wiley & Sons. 1905. pp. 261. Price, \$2.50.

Minet's monograph is a fairly complete enumeration and description of the different methods which have been suggested for the production of aluminium, and of the various chemical and industrial uses of the metal from the point of view of a practical inventor with some knowledge of thermo-chemistry; it is supplemented by a few statistical tables and a brief account, by the translator, concerning the production of aluminium in the United States.

The author gives many details of his own process, which, although it was once in use in France, has been abandoned, but his account of Héroult's or Hall's processes is brief. The former is used in Europe, the latter in Europe and in America.

At the present time the yearly output of aluminium is from 14,000,000 to 18,000,000 lbs., of which more than one-half is made by the Pittsburg Reduction Co., at Niagara Falls. The price is 31-37.5 c. per lb. here and 22 c. in Europe. E. R.

THE CONDUCTIVITY OF LIQUIDS. Methods, Results, Chemical Applications and Theoretical Considerations. By OLIN FREEMAN TOWER, PH.D., Assistant Professor of Chemistry, Western Reserve University, Easton, Pa.: Chemical Publishing Company. 1905. pp. 182. Price, \$1.50.

This useful little book contains just such information as one frequently desires to have at hand. About the only fault we can find with it is in the title. Conductivity of *Solutions* and

not of "Liquids" would have been more in accordance with the contents.

The author discusses such fundamental subjects as: Methods and Apparatus Used in Determining Conductivity; Dissociation of Electrolytes; Migration of Ions, both relative and absolute values; The Determination of μ_{∞} ; Influence of Temperature and Pressure on Conductivity; Solutions Containing Two Electrolytes; Non-aqueous Solutions and Conductivity of Electrolytes in Mixed Solvents. Useful tables of conductivity data are also appended.

The book is very well written, the style being clear, interesting and attractive. It is unfortunate that the contents could not have been brought a little nearer to the date of publication, but the reason for not doing so is given by the author in his preface.

It is to be hoped that the volume will have the wide circulation it deserves.

H. C. J.

EXPERIMENTAL ELECTROCHEMISTRY. By N. MONROE HOPKINS, PH.D., Assistant Professor of Chemistry in the George Washington University, Washington, D. C. With 130 illustrations. New York: D. Van Nostrand Company. 1905. pp. 284. Price, \$3.00 net.

It is stated in the preface that "It has been the aim of the author to produce a book that will prove useful in both the lecture room and the laboratory. Although a work upon the subject of electrochemistry must presuppose a working knowledge of chemistry and electricity, it has been the object of the writer to introduce the subject as clearly as possible, dealing with chemistry and electricity without assuming too much on the part of the student." Again, "Electrochemistry is at best a subject for the advanced student, and in order to carry out the experimental work with profit, as given here, he must have pursued beforehand laboratory courses in both chemistry and physics."

It will be recognized that this is a sound basis upon which to write a book on electrochemistry.

The first part of the book deals with the strictly scientific side of electrochemistry, while the second half has to do with more practical questions, such as the production of nitric acid from the air, the electrolytic production of the metals, the electric furnace and its products, the electrolytic preparation of organic compounds, primary and secondary cells, electricity from carbon, etc.

The style is clear and very readable. A few matters could be revised to advantage. Thus, on page 1, we find "basic experimental evidence." On page 48, the term "*molugram*"

is certainly not euphonious, and it is to be hoped will not find its way into physical-chemical literature.

The equation on page 108, in connection with the electrolysis of concentrated sulphuric acid, must not be accepted literally, since atomic oxygen is certainly not produced. Further, the use of the term "*heavy*" as applied to current will scarcely meet the demands of the purists.

In connection with the theory of the electrolysis of sulphuric acid, it is not pointed out with sufficient clearness that the older view is unquestionably wrong; and the newer view is not sufficiently elaborated. A few ions are not capable of carrying "many amperes," but many coulombs of electricity.

It will, of course, be recognized that these are minor matters, which can easily be corrected in a new edition.

The work, as a whole, is interesting and contains a number of ingenious experiments, some of which have important new features. It will doubtless find a good demand, especially in laboratories where considerable stress is laid upon electrochemistry. We wish it the success which it deserves.

H. C. J.

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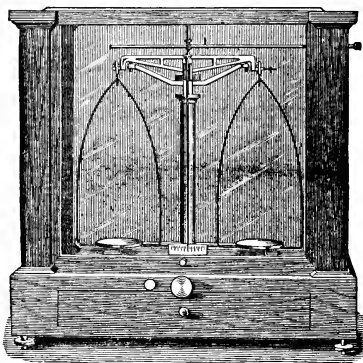
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C ₂ H ₆ ClAs. Cacodyl chloride. <i>Dehn and Wilcox</i>	1
C ₂ H ₇ Br ₂ As. Bromcacodyl hydrobromide. <i>Dehn and Wilcox</i>	15
C ₂ H ₇ Cl ₂ As. Chlorcacodyl hydrochloride. <i>Dehn and Wilcox</i>	16
C ₂ H ₇ I ₂ As. Iodocacodyl hydriodide. <i>Dehn and Wilcox</i>	17

C₃-GROUP.

3 III.

C ₃ H ₅ ON ₂ . Methyl cyaniminocarbonate. <i>Biddle</i>	347
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C₄-GROUP.

C ₄ H ₁₂ As ₂ . Cacodyl. <i>Dehn and Wilcox</i>	4
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3 IV.

C ₄ H ₈ O ₂ N ₂ . Methyl diimidooxalate. <i>Biddle</i>	347, 350
C ₄ H ₁₂ OAs ₂ . Cacodyl oxide. <i>Dehn and Wilcox</i>	4
C ₄ H ₁₂ ISb. Tetramethylstibonium iodide. <i>Dehn and Wilcox</i>	18

C₅-GROUP.

C ₅ O ₂ Br ₄ . Tetrabromcyclopenteneorthoquinone. <i>Jackson and Russe</i>	185
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3 V.

C ₅ H ₈ O ₂ N. Carbethoxyaminoacetonitrile. <i>Johnson and McCollum</i>	67
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C₆-GROUP.**3 VI.**

C ₆ H ₄ IAs. Trimethylallylarsonium iodide. <i>Dehn and Wilcox</i>	21
C ₆ H ₆ NBr ₂ . <i>o,p</i> -Dibrom- <i>o</i> -phenylenediamine. <i>Jackson and Russe</i>	150
C ₆ H ₇ NBr ₄ . <i>o,p</i> -Dibrom- <i>o</i> -phenylenediamine dihydrobromide. <i>Jackson and Russe</i>	152
C ₆ H ₁₂ O. Methyl isobutyl ketone. <i>Clarke and Shreve</i>	515
C ₆ H ₁₄ O. Methylisobutylcarbinol. <i>Clarke and Shreve</i>	515

4 VI.

C ₆ H ₇ O ₂ N ₂ Br. <i>p</i> -Brombenzoylurea. <i>Johnson and Jamieson</i>	307
C ₆ H ₇ NCIBr ₂ . <i>o,p</i> -Dibrom- <i>o</i> -phenylenediamine hydrochloride. <i>Jackson and Russe</i>	151

C₇-GROUP.

C ₇ H ₁₀ O ₅ . Ethyl oxomalonate. <i>Curtiss</i>	477
C ₇ H ₁₂ O ₆ . Ethyl dihydroxymalonate. <i>Curtiss</i>	478
C ₇ H ₁₄ S. Heptyl thiophane. <i>Mabery</i>	408

3 VII.

C ₇ H ₁₄ O ₂ S. Heptyl thiophane sulphone. <i>Mabery</i>	419
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4 VII.

C ₇ H ₇ O ₄ NS. <i>o</i> -Carbaminebenzenesulphonic acid. <i>Bradshaw</i>	335
C ₇ H ₇ O ₄ NS. <i>o</i> -Sulphaminebenzoic acid. <i>Bradshaw</i>	335
C ₇ H ₉ O ₅ NS. Acid ammonium salt of orthosulphobenzoic acid. <i>Cobb</i>	496

C₈-GROUP.

C ₈ H ₁₆ S. Octyl thiophane. <i>Mabery</i>	409
C ₈ H ₁₆ S. Isooctyl thiophane. <i>Mabery</i>	409

3 VIII.

C ₈ H ₁₆ SO ₂ . Octyl thiophane sulphone. <i>Mabery</i>	420
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4 VIII.

$C_8H_8O_2N_2S$. Benzenesulphonylaminoacetonitrile. <i>Johnson and McCollum</i>	58
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C₉-GROUP.

$C_9H_{12}O$. 1-Methyl-2-ethyl- α -furfuryl ethylene. <i>Hale, McNally and Pater</i>	72
$C_9H_{14}O_2$. Diethyl- α -furfuryl carbinol. <i>Hale, McNally and Pater</i>	72
$C_9H_{14}O_2$. Isocampholactone. <i>Noyes and Taveau</i>	385
$C_9H_{18}S$. Nonyl thiophane. <i>Mabery</i>	410

3 IX.

$C_9H_{18}O_2S$. Nonyl thiophane sulphone. <i>Mabery</i>	420
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4 IX.

$C_9H_9O_5SNa$. Sodium salt of ethyl orthosulphobenzoate. <i>Cobb</i> ..	489
$C_9H_{10}O_2N_2S$. Benzenesulphonylmethylaminoacetonitrile. <i>Johnson and McCollum</i>	59
$C_9H_{10}O_4NS$. Benzenesulphonylmethylaminoacetic acid. <i>Johnson and McCollum</i>	59

C₁₀-GROUP.

$C_{10}H_{20}S$. Decyl thiophane. <i>Mabery</i>	411
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3 X.

$C_{10}H_{10}NBr_2$. <i>o,p</i> -Dibrom- <i>o</i> -phenylenediacetamide. <i>Jackson and Russe</i>	152
$C_{10}H_{22}SAs$. Diisoamylarsine sulphide. <i>Dehn and Wilcox</i>	52
$C_{10}H_{23}O_2As$. Isoamylarsinic acid. <i>Dehn and Wilcox</i>	53

4 X.

$C_{10}H_6O_4Br_4$. Tetrabrompyrocatechin diacetate. <i>Jackson and Russe</i>	178
$C_{10}H_{10}O_4NS$. 2,6-Diketo-4-benzenesulphonylpiperazine. <i>Johnson and McCollum</i>	64
$C_{10}H_{12}O_2N_2S$. Benzenesulphonylaminoacetonitrile. <i>Johnson and McCollum</i>	60
$C_{10}H_{12}O_2N_2S$. <i>p</i> -Methoxybenzoylpseudomethylthiourea. <i>Johnson and Jamieson</i>	308
$C_{10}H_{13}O_4NS$. Benzenesulphonylaminoacetic acid. <i>Johnson and McCollum</i>	61
$C_{10}H_{22}ClBrAs$. Diisoamylarsine chlordibromide. <i>Dehn and Wilcox</i>	51

C₁₁-GROUP.

C ₁₁ H ₁₂ O ₂ . δ-Phenyl-Δ ^a -pentenoic acid. <i>Michael and Garner</i>	258
C ₁₁ H ₂₂ S. Undecyl thiophane. <i>Mabery</i>	411

3 XI.

C ₁₁ H ₂₂ O ₂ S. Undecyl thiophane sulphone. <i>Mabery</i>	421
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4 XI.

C ₁₁ H ₁₂ O ₄ N ₂ S. Benzenesulphonylcarbethoxyaminoacetonitrile. <i>Johnson and McCollum</i>	61
C ₁₁ H ₁₄ O ₂ N ₂ S. Benzenesulphonyl- <i>n</i> -propylaminoacetonitrile. <i>Johnson and McCollum</i>	61
C ₁₁ H ₁₅ O ₄ NS. Benzenesulphonyl- <i>n</i> -propylaminoacetic acid. <i>Johnson and McCollum</i>	61
C ₁₁ H ₁₅ O ₄ NS. Ethyl benzenesulphonylmethylaminoacetic acid. <i>Johnson and McCollum</i>	60

C₁₂-GROUP.

C ₁₂ H ₂₆ . Dimethyldiisobutylethane. <i>Clarke and Shreve</i>	519
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2 XII.

C ₁₂ H ₂₀ O ₂ . Methylisobutylpinacone. <i>Clarke and Shreve</i>	517
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3 XII.

C ₁₂ HO ₄ Br ₇ . Heptabromorthoquinopyrocatechin hemiether. <i>Jackson and Russe</i>	165, 166, 167
C ₁₂ H ₄ O ₅ Br ₈ . Octobromorthoquinhydrone. <i>Jackson and Russe</i> ..	173
C ₁₂ H ₁₀ Br ₃ As. Diphenylarsine tribromide <i>Dehn and Wilcox</i>	48
C ₁₂ H ₁₀ IAS. Diphenylarsine iodide. <i>Dehn and Wilcox</i>	48
C ₁₂ H ₁₁ O ₂ As. Diphenylarsinic acid. <i>Dehn and Wilcox</i> ..	41
C ₁₂ H ₂₄ O ₂ S. Dodecyl thiophane sulphone. <i>Mabery</i>	421

4 XII.

C ₁₂ H ₁₄ O ₄ N ₂ S. 2-Ethoxy-4-benzenesulphonyl-6-ketopiperazine. <i>Johnson and McCollum</i>	65
C ₁₂ H ₁₄ O ₄ N ₂ S. Ethyl benzenesulphonylcyanmethylaminoacetate. <i>Johnson and McCollum</i>	63

C₁₄-GROUP.

C ₁₄ H ₂₈ S. Quatdecyl thiophane. <i>Mabery</i>	413
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4 XIV.

C ₁₄ H ₁₆ O ₃ N ₂ Cl ₃ . Addition product of trichlororesorcinol and <i>p</i> -nitro-sodimethylaniline. <i>Torrey and Gibson</i>	250
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C₁₅-GROUP.

4 XV.

C ₁₅ H ₁₂ O ₃ N ₂ S. Benzenesulphonylbenzoylaminoacetonitrile. <i>Johnson and McCollum</i>	66
C ₅ H ₁₃ O ₄ N ₃ S. Benzenesulphonyl- <i>p</i> -nitrobenzylaminoacetic acid. <i>Johnson and McCollum</i>	63
C ₁₅ H ₁₄ O ₂ N ₂ S. Benzenesulphonylbenzylaminoacetonitrile. <i>Johnson and McCollum</i>	62
C ₁₅ H ₁₄ O ₆ N ₂ S. Benzenesulphonyl- <i>p</i> -nitrobenzylaminoacetic acid. <i>Johnson and McCollum</i>	63
C ₁₅ H ₁₅ O ₄ NS. Benzenesulphonylbenzylaminoacetic acid. <i>Johnson and McCollum</i>	62

C₁₆-GROUP.

C ₁₆ H ₃₂ S. Sexdecyl thiophane. <i>Mabery</i>	413
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4 XVI.

C ₁₆ H ₁₄ O ₂ N ₂ S. Symmetrical dibenzoylpseudomethylthiourea. <i>Johnson and Jamieson</i>	303
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5 XVI.

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C₁₇-GROUP.

C ₁₇ H ₁₄ O ₂ . Diphenyl- α -furfuryl carbinol. <i>Hale, McNally and Pater</i>	70
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4 XVII.

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C₁₈-GROUP.

C ₁₈ H ₁₀ O ₂ . Methyl ether of diphenyl- α -furfuryl carbinol. <i>Hale, McNally and Pater</i>	71
C ₁₈ H ₁₉ N. Methyl diphenylvaleronitrile. <i>Kohler</i>	396
C ₁₈ H ₂₀ O. 3,4-Diphenylhexanone-2. <i>Kohler</i>	399
C ₁₈ H ₃₆ S. Octodecyl thiophane. <i>Mabery</i>	413

4 XVIII.

$C_{18}H_{16}O_4N_2S$. Symmetrical diparamethoxybenzoylpseudomethylthiourea. <i>Johnson and Jamieson</i>	308
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 C_{19} -GROUP.

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3 XIX.

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 C_{20} -GROUP.

$C_{20}H_{20}O_2$. Methyl ether of dibenzyl- α -furfuryl carbinol. <i>Hale, McNally and Pater</i>	74
$C_{20}H_{14}OAs$. Isoamylcacodylic oxide. <i>Dehn and Wilcox</i>	50

3 XX.

$C_{20}H_{10}N_2Br_2$. <i>o,p</i> -Dibromdiphenylenequinoxaline. <i>Jackson and Russe</i>	153
$C_{20}H_{12}N_2Br_2$. <i>o,p</i> -Dibromdiphenylenequinoxaline. <i>Jackson and Russe</i>	153

4 XX.

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 C_{21} -GROUP.

$C_{21}H_{17}N$. Triphenylpropionitrile. <i>Kohler</i>	401
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$C_{22}H_{22}O_7N_2$. Addition product of salicylic acid and <i>p</i> -nitrosodimethylaniline. <i>Torrey and Gibson</i>	250
$C_{22}H_{26}O_4N_4$. Addition product of <i>p</i> -nitrosodimethylaniline and pyrocatechol. <i>Torrey and Gibson</i>	252

4 XXII.

$C_{22}H_{23}O_4N_4Br_3$. Addition product of <i>p</i> -nitrosodimethylaniline and tribromresorcinol. <i>Torrey and Gibson</i>	251
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C₂₃-GROUP.

C ₂₂ H ₂₁ N. Ethyltriphenylpropionitrile. <i>Kohler</i>	402
C ₂₃ H ₂₂ O. Diphenylvalerophenone. <i>Kohler</i>	399

C₂₄-GROUP.

C ₂₄ H ₂₅ N. Benzylidiphenylvaleronitrile. <i>Kohler</i>	396
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C₃₀-GROUP.

C ₃₀ H ₂₄ O ₃ . Tetraphenyl- α, α' -furfuryl dicarbinol. <i>Hale, McNally</i> and <i>Pater</i>	74
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C₃₂-GROUP.

C ₃₂ H ₂₈ O ₄ . Methyl ether of tetraphenyl- α, α' -furfuryl dicarbinol. <i>Hale, McNally</i> and <i>Pater</i>	75
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C₃₃-GROUP.

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C₃₄-GROUP.

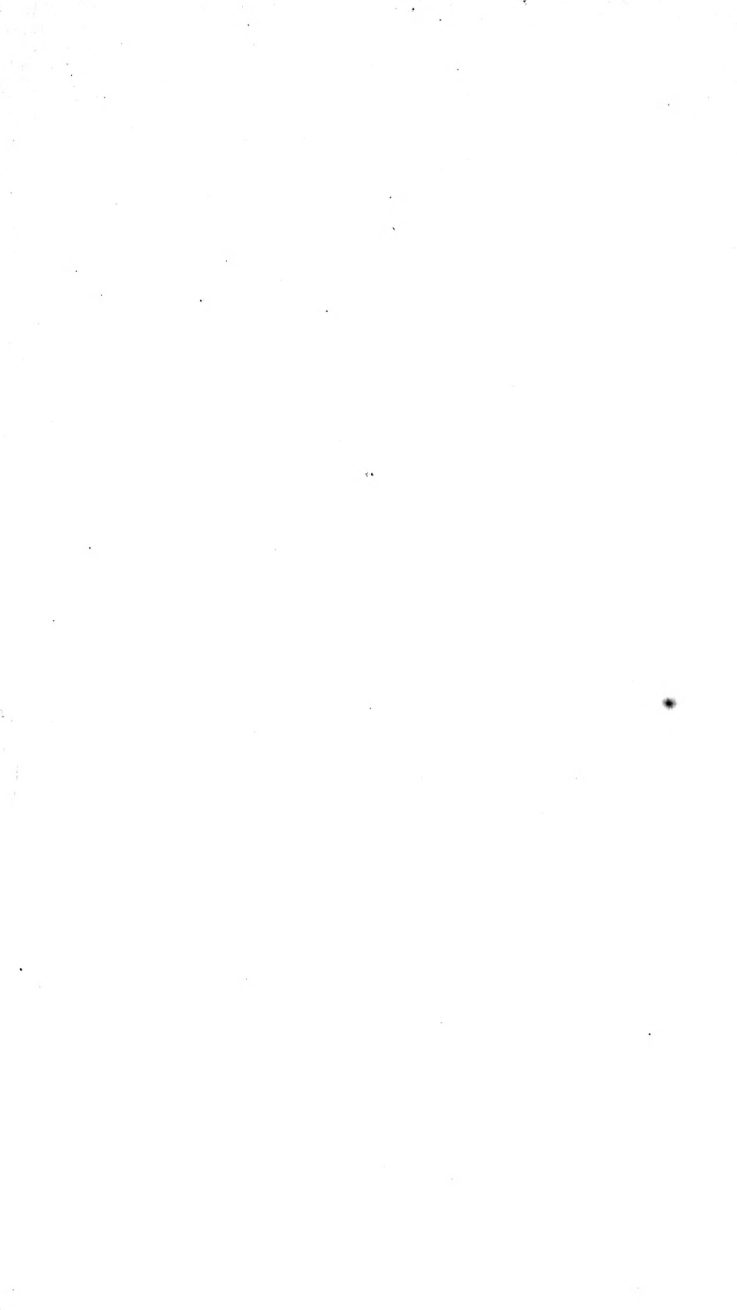
C ₃₄ H ₃₂ O ₃ . Ethyl ether of tetraphenyl- α, α' -furfuryl dicarbinol. <i>Hale, McNally</i> and <i>Pater</i>	76
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ERRATA.

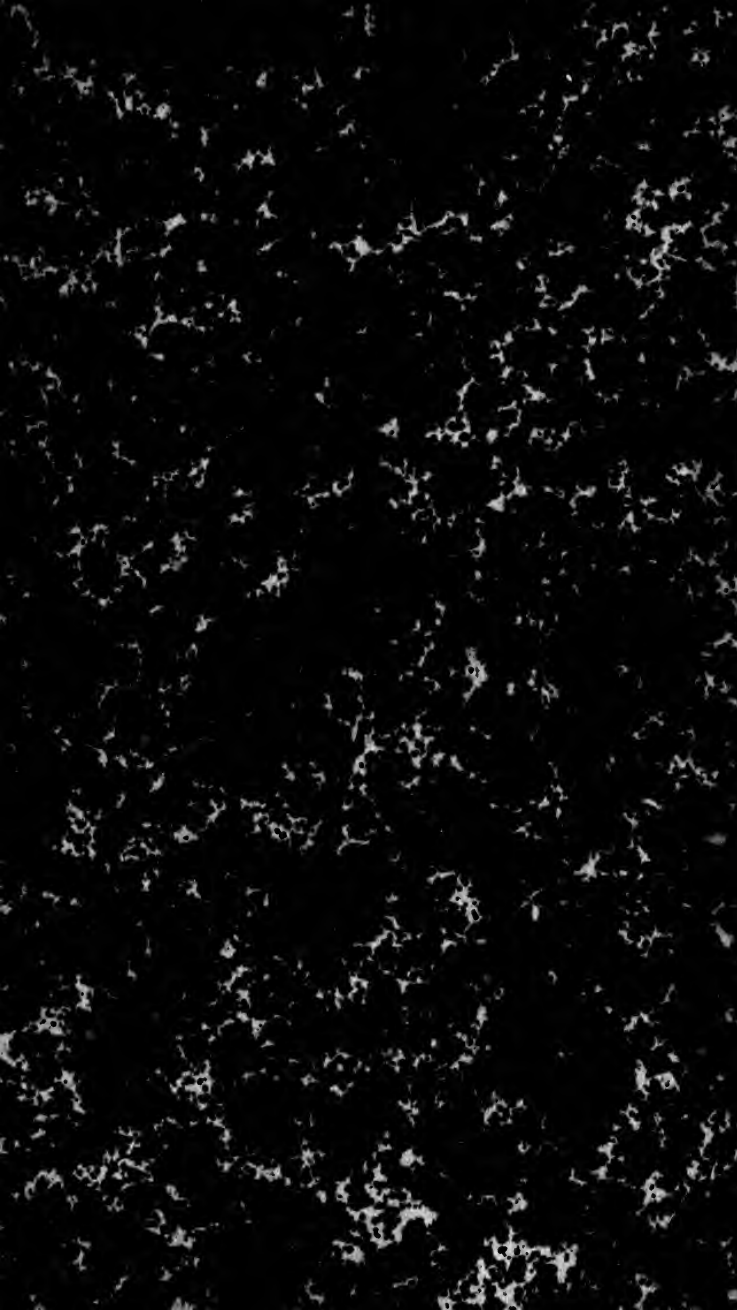
✓	Vol. 33,	page 336,	line 7.	The last formula should be $C_6H_5CHRC(CN) : C(OC_2H_5)OMgBr.$		
✓	"	35,	page 96,	line 20,	for Mallett read Mallet.	
✓	"	"	"	"	6 ¹	methodes read méthodes.
✓	"	"	"	"	"	novelles read nouvelles.
✓	"	"	"	"	"	appliquees read appliquées.
✓	"	"	"	97	11	Baunhauer read Baumhauer.
✓	"	"	"	97	10	neuerer read neuere.
✓	"	"	"	187	9 ¹	late Billitzer read later Billitzer.
✓	"	"	"	292	3 ¹	<i>i. e.</i> read in.
✓	"	"	"	342	11 ¹	aniline orthosulphonic read anilineortho- sulphonic.
✓	"	"	"	379	8	Rene read Renè.
✓	"	"	"	468	10	Baumberger's read Bamberger's.
✓	"	"	"	472	20 ¹	ZN read Zn.

¹ From foot.









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